

5418/- 15

Reference



82

## TO THE READER

**K**INDLY use this book very carefully. If the book is disfigured or marked or written on while in your possession the book will have to be replaced by a new copy or paid for. In case the book be a volume of set of which single volumes are not available the price of the whole set will be realized.

# AMARSINGH COLLEGE



Checked

1976

81

Library

Checked

85

Class No.

541-3

Book No.

G 54R

Acc. No.

6389 ✓





# **RECENT ADVANCES IN PHYSICAL CHEMISTRY**



1077  
A/N. 61.

# RECENT ADVANCES IN PHYSICAL CHEMISTRY

BY

**SAMUEL GLASSTONE**

Ph.D., D.Sc. (Lond.), F.I.C.

*Lecturer in Physical Chemistry at the  
University of Sheffield*

With 31 Illustrations

THIRD EDITION

LONDON

**J. & A. CHURCHILL LTD.**

104 GLOUCESTER PLACE

PORTMAN SQUARE

*Reprinted*

1938

63-7  
10/1/44  
2.5

To V. 10/1/44

<i>First Edition</i>	.	.	.	1931
<i>Second Edition</i>	.	.	.	1933
<i>Third Edition</i>	.	.	.	1936
<i>Reprinted</i>	.	.	.	1938



## PREFACE TO THIRD EDITION

THE most important new matter in this edition is a long section on the application of quantum mechanics to problems of valency and molecular structure, including an account of the important phenomenon which has become generally known under the name of "resonance." The treatment is essentially non-mathematical, and it has been the object of the author to give, as far as possible, the physical and chemical significance of the results obtained by the methods of wave mechanics. A section on the use of electronic term formulæ and the representation of electronic configurations in molecules, essential for the understanding of the method of molecular orbitals, has been written and the influence of solvent on dipole moment has been treated at greater length than in the earlier editions. Every chapter has been revised and, in addition to the provision of new material, some portions of the book have been re-written and others re-arranged as an aid to clarity. The chapter on "Solubility," omitted from the second edition, and that on "Acid-Base and Salt Catalysis," which has been left out of this one on account of requirements of space, have been included in the new companion volume "Recent Advances in General Chemistry," as they fit in better with the general scope of that work. Thanks are due to Dr. A. Farkas and the Royal Society for loan of a block, and to the author's wife for her help in many ways.

S. G.

SHEFFIELD.

## EXTRACT FROM PREFACE TO FIRST EDITION

ALTHOUGH the discoveries in physical chemistry reported during the past decade have not been as spectacular as those of the two which immediately preceded it, yet considerable progress has been made in many directions. It is too soon, however, for the new view-points to be incorporated in the ordinary text-books of physical chemistry, and it is with the object of bridging the gap between these and the extensive journal literature that the present book has been written. Its appeal is directed more particularly to two types of readers: firstly, to those chemists who, having started on a professional career, after completing a University course, find that they have neither time nor opportunity to keep in touch with modern developments in physical chemistry; and, secondly, to students still at the University who are confronted with an ever-increasing volume of material which must be learnt for its own intrinsic value, as well as for examination purposes.

It is the general experience of chemistry teachers at the Universities that time does not permit them, even if it were thought desirable, to lecture on all aspects of physical chemistry, and so a great deal must be left to the students' own reading. This is, of course, an essential part of the University training, but the author's experience has led him to think that a guide to the literature, in the form of a general survey of each particular subject together with a list of references, would be a valuable help to the student. It is hoped that the present book will fulfil, to some extent at least, this requirement.

The order of the chapters is to some extent arbitrary, although as far as possible the arrangement is such that special information required in any chapter will be found in a preceding one. Each chapter is, however, self-contained, and may be studied in any



## PREFACE

vii

desired order; frequent cross-references are inserted in order to avoid possible difficulties. The treatment is critical throughout, and wherever feasible the author has attempted to give the reader a lead through controversial subjects.

The task of writing this book has been considerably diminished by the use of the following monographs: "The Electronic Theory of Valency" (Sidgwick); "The Parachor and Valency" (Sugden); "Polar Molecules" (Debye); "Photo-processes in Gaseous and Liquid Systems" (Griffith and McKeown); "Kinetics of Chemical Change in Gaseous Systems" (Hinshelwood); "Physics and Chemistry of Surfaces" (Adam); and "Surface Chemistry" (Rideal). To their writers the author must express his indebtedness, as well as to Dr. N. K. Adam and Dr. A. Elliott for permission to reproduce figures.

S. G.

SHEFFIELD,

August, 1931.

## EXTRACT FROM PREFACE TO SECOND EDITION

It has been necessary to revise every chapter for the present edition and to include a large amount of fresh material; the more important new subjects now discussed are as follows: wave mechanics and its applications to problems of valency and the calculation of energy of activation; nuclear disintegration and the discovery of the neutron and the positive electron; the influence of free and restricted rotation on dipole moments; molecular beams and their uses; potential energy curves; atomic reactions; the kinetics of photochemical reactions; activated and discontinuous adsorption; surface potentials; and the mobility of surface molecules.

S. G.

SHEFFIELD,

August, 1933.

# CONTENTS

CHAP.		PAGE
	PREFACE . . . . .	V
I.	THE ELECTRONIC THEORY OF VALENCY . . . . .	1
II.	THE PARACHOR . . . . .	98
III.	DIPOLE MOMENTS . . . . .	127
IV.	MOLECULAR SPECTRA . . . . .	188
V.	HOMOGENEOUS GAS REACTIONS . . . . .	260
VI.	PHOTOCHEMICAL REACTIONS . . . . .	319
VII.	THE PROPERTIES OF SURFACES . . . . .	346
VIII.	HETEROGENEOUS CATALYSIS . . . . .	394
IX.	STRONG ELECTROLYTES . . . . .	438
	INDEX . . . . .	471



# RECENT ADVANCES IN PHYSICAL CHEMISTRY

## CHAPTER I

### ATOMIC STRUCTURE AND THE THEORY OF VALENCY

IN reviewing recent progress in chemistry there is little doubt that one particular advance, namely the electronic theory of valency, transcends all others in importance. It has permitted chemical reactions and the structure of molecules to be studied from a new viewpoint, which has not only been very fruitful of results, but has also produced a remarkable unification of existing data. Since in the majority of the chapters in this book there will be occasion to refer, directly or indirectly, to matters connected with molecular structure, it will perhaps be appropriate to commence with a short introduction to the electronic theory of valency.

### THE STRUCTURE OF THE ATOM

The theory was developed from, and is closely connected with, the modern ideas concerning the structure of the atom, and so a short digression to review this latter aspect of the problem is first necessary. In 1911 Rutherford established, as a result of his experiments on the scattering of  $\alpha$ -particles, that an atom of matter consisted of a very small positively charged nucleus containing nearly the whole of the mass, surrounded by a number of negatively charged particles, or electrons. Recent progress in wave mechanics has made it almost impossible to give an exact physical idea of an electron, but it will be shown later (p. 54) that with certain limitations it may still be regarded as if it were a



unit "particle" of negative electricity, associated with a train of "electron waves"; the chemist may, therefore, still speak of the electrons surrounding the positive nucleus of an atom. Since the atom as a whole is electrically neutral, it follows that the number of electrons outside the nucleus, generally called "orbital electrons," or better, "extra-nuclear electrons," must be equal to the net number of unit positive charges on the nucleus. This number has been identified with the atomic number of the element: that is, its number when the elements are placed in the order of the periodic classification. As the atomic number increases from element to element throughout the periodic table, so also does the number of extra-nuclear electrons; hydrogen, the lightest element, has one outer electron only, whereas uranium with an atomic number of ninety-two has that number of electrons. Although chemists realised that the arrangement of these electrons was connected with the chemical properties of the elements, and physicists knew that this arrangement accounted for the various spectra, both X-ray and visible, which a particular element produced, for several years there was no definite suggestion forthcoming as to the details of electronic structure. It was known, from the different types of X-ray spectra, that there were different electronic groups, or levels, in the atom, but the number of electrons in each level was uncertain.

**The Arrangement of Electrons—Langmuir's Theory.** After various tentative suggestions had been made by different authors Langmuir produced in 1919 the first comprehensive scheme of electronic architecture; he started off with the fundamental idea that the inert gases of the atmosphere (Group O) represented the most stable electronic arrangements, and hence contained completed electronic groups (shells, sheaths or layers). The atomic numbers, and consequently the number of extra-nuclear electrons, of these gases are given in Table I.

The difference in the number of electrons for successive members of this series was taken by Langmuir to represent the number of electrons contained in successive shells; these were, therefore, assumed to be 2, 8, 8, 18, 18 and 32. There appears, at first sight, to be no regularity amongst these numbers, but Rydberg (1914)



TABLE I.—Atomic Numbers of the Inert Gases

Element.	Atomic Number.			Difference.
Helium . . . . .	2	..	2	
Neon. . . . .	10	..	8	
Argon . . . . .	18	..	8	
Krypton . . . . .	36	..	18	
Xenon . . . . .	54	..	18	
Emanation. . . . .	86	..	32	

had previously shown that they may be expressed by the equation :

$$N = 2(1^2, 2^2, 2^2, 3^2, 3^2, 4^2),$$

and so they may well have had the important significance attributed to them by Langmuir. According to this author's theory the increasing number of electrons, with increasing atomic number, filled up the series of shells commencing with the first ; as each shell was completed with an inert gas, *and not before*, the next shell commenced to form with an alkali metal. On the basis of these views Langmuir was able to account for the variation of properties throughout the periodic classification, for the presence of the transition elements (Group VIII.) when the shell of eighteen electrons succeeded the two groups of eight, and the incidence of the rare-earth series of elements when the shell of thirty-two electrons was developing. It was considered that the first eighteen of this group of thirty-two were arranged in such a manner as to imitate the two layers of eighteen electrons immediately below, but that at the nineteenth electron a new type of arrangement was necessary. From this point of view it would be expected that the element of atomic number  $2 + 8 + 8 + 18 + 18 + 18 (= 72)$  should be the last of the series preceding it : that is, the last of the rare-earth group ; at the time (1919) Langmuir believed the element of atomic number 72 to be the rare-earth element lutecium, but this view was later shown to be incorrect.

**The Bohr-Bury Theory.** In 1921 Bury put forward a modification of the Langmuir arrangement which appeared to be in better agreement with the physical and chemical properties of



certain elements; it was suggested that the maximum number of electrons which each shell could contain was proportional to the area of its surface, and that successive layers, therefore, would contain 2, 8, 18 and 32 (*i.e.*,  $2 \times 1^2$ ,  $2 \times 2^2$ ,  $2 \times 3^2$  and  $2 \times 4^2$ ) electrons. Further, Bury considered that the maximum number of electrons in the *outer* layer of an atom was eight, and that more than this number could exist in a shell only when there were electrons in an outer layer. In the modified theory it was consequently not necessary for a sheath to be complete before another commenced to be formed; in fact a new layer had to be started whenever the hitherto outermost sheath attained eight electrons. While the fourth sheath was developing, however, electrons could enter the third layer and increase it up to eighteen, instead of remaining at eight as Langmuir considered; in the same way the fourth sheath could be increased eventually up to thirty-two electrons, but this only occurred when the fifth and sixth sheaths were quite well developed. According to the views of Bury the inert gases of Group O were supposed to have the structures given in Table II.

TABLE II.—*Electronic Structures of Inert Gases according to Bury*

Element.	Atomic Number.	Electron Shells.					
		1st.	2nd.	3rd.	4th.	5th.	6th.
Helium . . .	2	2	—	—	—	—	—
Neon . . .	10	2	8	—	—	—	—
Argon . . .	18	2	8	8	—	—	—
Krypton . . .	36	2	8	18	8	—	—
Xenon . . .	54	2	8	18	18	8	—
Emanation . . .	86	2	8	18	32	18	8

In order to illustrate further the application of the theory the first long period of the classification of elements may be considered; the first member of this series, potassium, would have the same electronic arrangement as proposed by Langmuir, 2, 8, 8, 1, and so also would calcium 2, 8, 8, 2, and scandium 2, 8, 8, 8; but with titanium Bury supposed that the third sheath would commence



to increase, thus 2, 8, 9, 8, whereas Langmuir had suggested 2, 8, 8, 4. The difference between the two theories is well brought out in connection with the rare-earth group; according to Bury the first element of the series, lanthanum, has the electronic structure 2, 8, 18, 18, 9, 2, and successive members gradually build up the fourth layer until it contains its maximum number of thirty-two electrons. The last rare-earth element should have electron sheaths containing 2, 8, 18, 32, 9, 2, respectively, that is a total of 71 electrons; the known element, lutecium, should thus be the last of the series with an atomic number of 71, and the element number 72 should not be a rare-earth, but a homologue of zirconium.

At about the same time as Bury developed his theory on chemical grounds Bohr (1921) published independently an almost identical theory of the arrangement of the extra-nuclear electrons, based on a study of the emission spectra of the elements. In each case the inert gases were considered to have eight electrons in their outermost layers, and the element of atomic number 72 was regarded as a homologue of zirconium, and not, as Langmuir considered, a rare-earth. In order to decide this matter Coster and Hevesy (1922) examined the characteristic X-rays from a number of zirconium minerals, and found in almost every case a distinct line corresponding in frequency to that expected from an element of atomic number 72. Further, by suitable chemical means it was possible to extract from such minerals appreciable amounts of the new element, which was called "hafnium"; it resembled zirconium very much in its properties, and was so difficult to separate from it that many specimens of zirconium compounds, previously believed to be quite pure, were shown to contain up to 5 per cent. of hafnium. The new element was definitely not a member of the rare-earth series, and so the evidence was in favour of the Bohr-Bury arrangement of electrons, rather than that of Langmuir.

**Bohr's Theory of Atomic Spectra.** In order to account for the spectra of elements Bohr (1913) had suggested that each extra-nuclear electron was capable of moving in one of a definite number of possible orbits; as long as it remained in one orbit radiation



was neither absorbed nor emitted, but when the transition occurred from one orbit to another radiation of definite frequency was produced. For each orbit in which electrons could move the atom was supposed to possess a definite energy content, and when the electron passed from an orbit for which the energy of the atom was  $E'$  to one corresponding to an energy of  $E''$ , then  $E' - E''$  energy would be emitted in the form of radiation as a spectral line of frequency  $\nu$ , given by the quantum theory that

$$E' - E'' = h\nu,$$

where  $h$  is the Planck constant,  $6.547 \times 10^{-27}$  erg-second. The energy of the atom corresponding to each electronic orbit was expressed in terms of a "principal quantum number" ( $n$ ), the value of which was a small integer. On the basis of this theory Bohr was able to account in a very satisfactory manner for the main lines in the spectrum of the hydrogen atom and of ionised helium.

**Quantum Numbers.** The principal quantum number, which had been postulated arbitrarily by Bohr to fit in with the experimental results, now follows as a necessity of the wave aspect of the electron (p. 56). Solution of the appropriate equation of wave mechanics shows that an atom can only possess certain definite energy values, corresponding to the energies of Bohr's possible electronic orbits; the concept of non-radiating stationary orbits is, however, no longer necessary and it is replaced by the idea of a series of electronic "energy levels" for the atom. The transition of an electron from one level to another results in the production of a definite spectral line, the frequency of which is determined by the fundamental equation of the quantum theory.

In order to account for the fine structure, or multiplicity, of the spectral lines and for the behaviour of the spectrum in a magnetic field (Zeemann effect), it is necessary to introduce three subsidiary quantum numbers, which define the energy sub-levels, in addition to the principal quantum number ( $n$ ) defining the main energy level. The principal quantum number has been identified with the number of the electron sheath, thus the first shell with two electrons is called the first quantum group ( $n = 1$ ); the second



shell capable of containing eight electrons only is the second quantum group ( $n = 2$ ), and the third shell, which may be occupied by eighteen electrons, is termed the third quantum group ( $n = 3$ ), and so on. These shells are sometimes referred to by the letters  $K$  ( $n = 1$ ),  $L$  ( $n = 2$ ),  $M$  ( $n = 3$ ), etc., since the electrons contained in them are believed to be responsible for the characteristic X-rays distinguished by the same letters. The necessity for assuming subsidiary quantum numbers implies that each quantum group may be divided into a number of sub-groups; to each of these sub-groups is given an "orbital" quantum number. This is generally represented by  $l$ , and may have several possible values, varying from  $l = 0$  to  $n - 1$ ; hence the number of sub-groups in any main group is equal to the principal quantum number of the main group. Thus the first quantum group ( $n = 1$ ; 2 electrons) has one sub-group, which is equivalent to saying that no subdivision is necessary and all electrons are at the same level; in the second quantum group ( $n = 2$ ; 8 electrons), the electrons are divided into two sub-groups ( $l = 0$  and 1); the third quantum group ( $n = 3$ ; 18 electrons) has three sub-groups ( $l = 0, 1$  and 2), and so on. The electrons in any group having the quantum number  $l = 0$  are often called  $s$  electrons, when  $l = 1, 2$  or 3, they are termed  $p, d$  and  $f$  electrons, respectively; these letters are the initials of the words "subsidiary," "principal," "diffuse" and "fundamental" which are used in describing spectral series connected with the corresponding  $l$  values. Electrons in higher groups are called  $g$  and  $h$ , for  $l = 5$  and 6.

**The Pauli Principle.** Originally Bohr considered that the total number of electrons in a main group was divided equally between the sub-groups: for example, in the fourth quantum group (32 electrons) there are four sub-groups, and each was supposed to contain 8 electrons when complete; this idea was later shown to be incorrect. The number of electrons in each of the various sub-groups is determined by two further quantum numbers, called the "magnetic" ( $m$ ) and "spin" ( $s$ ) quantum numbers, respectively, and by the "exclusion principle" enunciated by Pauli (1925); according to this principle no two



## 8 THE ELECTRONIC THEORY OF VALENCY

electrons in the same atom may have the same four quantum numbers. The study of spectra leads to the conclusion that  $m$  may be zero or any integer between  $+l$  and  $-l$ , inclusive, but  $s$  can only be  $+\frac{1}{2}$  or  $-\frac{1}{2}$ , to represent spins in one direction or the opposite. Having regard to these limitations, and that already mentioned for the quantum number  $l$ , the Pauli principle leads to the following distribution among the subsidiary quantum groups when the principal quantum numbers are 1 and 2, that is in the first two main groups of electrons :—

First Quantum Group ( $n = 1$ ).			Second Quantum Group ( $n = 2$ ).							
$l$	0	0	$l$	0	0	1	1	1	1	1
$m$	0	0	$m$	0	0	-1	-1	0	0	1
$s$	$+\frac{1}{2}$	$-\frac{1}{2}$	$s$	$+\frac{1}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$
Total :	2			8						

The first quantum group thus contains two  $s^*$  electrons ( $l = 0$ ), whereas the second group contains two  $s$  and six  $p$  electrons. The first two groups can thus contain only two and eight electrons respectively; this is in harmony with the theory of electronic arrangement proposed by Langmuir and by Bohr and Bury. In the third quantum group ( $n = 3$ ),  $l$  may be 0, 1 or 2; if  $l = 0$ ,  $m$  can only be 0, and  $s$  is  $+\frac{1}{2}$  or  $-\frac{1}{2}$ , and so there are only two electrons in the first sub-group; if  $l = 1$ ,  $m$  may be  $+1$ ,  $-1$  or 0, and  $s$  can be  $+\frac{1}{2}$  or  $-\frac{1}{2}$  in each case, making a total of six electrons possible in the second sub-group; if  $l = 2$ ,  $m$  may be  $+2$ ,  $-2$ ,  $+1$ ,  $-1$  or 0, and  $s$  is  $+\frac{1}{2}$  or  $-\frac{1}{2}$  in each case, and so there are ten ( $d$ ) electrons possible in the third sub-group. Hence by the Pauli exclusion principle the maximum number of electrons permissible in the third quantum group is 18; in the same manner it can be shown that in the fourth quantum group 32 electrons (*i.e.*, 2, 6, 10, 14) may be present. These results are in striking agreement with the main Bohr-Bury theory, but show that Bohr's suggestion of the equal division of the electrons between the sub-groups is probably not correct.

It is interesting to mention that even before the Pauli principle

\* It is necessary to avoid confusion between the use of  $s$  as applied to an electron for which  $l=0$ , and its use to designate the spin quantum number.



had been enunciated, Main Smith (1922) and Stoner (1924), from chemical and physical evidence respectively, had put forward suggestions concerning the arrangement of the electrons within the sub-groups; the maximum numbers which these authors proposed are almost identical with those to be expected from the exclusion principle.

## ELECTRONIC CONFIGURATIONS OF ATOMS AND MOLECULES

An electron in an atom is designated by an integer, which is the principal quantum number  $n$ , and a letter representing the value of  $l$ ; thus a  $1s$  electron is one for which  $n = 1$  and  $l = 0$ ;  $3d$  is an electron for which  $n = 3$  and  $l = 2$ , and so on. The number of electrons in an atom having the same values of  $n$  and  $l$  is indicated by a suffix: thus,  $2p^6$  means that in the given atom there are six electrons for which  $n = 2$  and  $l = 1$ ; this is, of course, the maximum number of  $p$  electrons in any quantum level. The carbon atom in its lowest energy, or ground, state has the electronic configuration  $1s^2 2s^2 2p^2$ , whereas silicon would be represented by  $1s^2 2s^2 2p^6 3s^2 3p^2$ . In the excited states, involved in the production of electronic spectra (Chapter IV.), the electrons are arranged differently: thus, a well known state of carbon is  $1s^2 2p^4$ , the two  $2s$  electrons having been raised to the  $2p$  level.

**Atom Terms.** The electronic state, or "term," of an atom is represented by the aid of the resultant orbital angular momentum  $L$ , and the resultant spin  $S$ . An atom may have a number of different  $L$  values, which are determined by the quantum number  $l$  of electrons other than those in completed groups, or "closed shells"; as already indicated, completed groups are  $1s^2$ ,  $2s^2$ ,  $2p^6$ , etc. For two electrons in incompleted groups, having orbital quantum number  $l_1$  and  $l_2$ , respectively,

$$L = l_1 + l_2, l_1 + l_2 - 1, \dots, l_1 - l_2;$$

if there are three electrons, then the series of  $L$  values is given by adding  $l_3$  to, or subtracting it from, the figures for two electrons. The atomic terms are called  $S$ ,  $P$  or  $D$ , according as the value of  $L$  is 0, 1 or 2. For the ground state of the carbon atom, mentioned above, there are only two  $2p$  electrons not in closed shells, and since



for both of these  $l = 1$ , the possible  $L$  values are 2, 1 and 0, and the three terms  $D$ ,  $P$  and  $S$ , respectively, are therefore implied. When an atom has all its electrons in closed shells,  $L$  is of course zero, and so it must have an  $S$  term.

In order to particularise further, the "multiplicity," which determines the number of lines constituting the fine structure of any main line in the atomic spectrum, is included; this is given by  $2S + 1$ , where  $S$  is here the resultant spin, and is equal to the algebraic sum of the spin numbers of the electrons not in complete groups. Since the spin numbers can be only  $+\frac{1}{2}$  or  $-\frac{1}{2}$ , the  $S$  values for two electrons are either 0 or 1, and for three either  $\frac{1}{2}$  or  $\frac{3}{2}$ , and so on. The multiplicity is inserted as a prefix to the term letter, in the form of a superscript. The  $2p$  electrons in the ground state of carbon can give a resultant spin of zero or unity, so that the corresponding multiplicities would be 1 and 3, respectively: the various possible states are, therefore,  $^1D$ ,  $^3D$ ,  $^1P$ ,  $^3P$ ,  $^1S$  and  $^3S$ . Certain rules have been developed for determining which of a number of terms is the "deepest," that is to say, has the lowest energy, and so represents the ground state: in general, the greater the multiplicity and the  $L$  value the lower the term. For the case under consideration  $^3D$  should be the lowest, but this is "forbidden," for other reasons, and so the ground state of the carbon atom has a  $^3P$  term. The excited state, to which reference was made previously, is a  $^5S$  state which means that the resultant spin is 2, and so all four  $2p$  electrons have spins in the same direction; the importance of this point will be considered later. Other symbols are used to characterise atomic terms more completely, but they need not concern us here, although they are of great importance in spectroscopy.

**Electron Configuration in Molecules.** A nomenclature similar to that employed for atoms can be used if the molecule has central symmetry: this is achieved artificially by imagining the atomic nuclei to approach one another until they nearly fuse, and the system then becomes almost a "united atom." The notation employed is strictly speaking only justifiable for diatomic molecules. The quantum numbers  $n$  and  $l$ , which have the same significance as for an atom, are used, and  $l$  can have the series of



values 0 to  $n - 1$ ; the  $s, p, d, f$  notation, for  $l = 0, 1, 2, 3$ , respectively, is also retained. In addition there is used the "axial" quantum number  $\lambda$ , which is the component of  $l$  along the internuclear axis; it can have any of the values  $l, l - 1, \dots, -l$ . Frequently it is only the numerical value of  $\lambda$  which is important and not the sign, and the Greek letters,  $\sigma, \pi, \delta$ , are used for  $\lambda$  values of 0,  $\pm 1$ ,  $\pm 2$ , respectively. The spin quantum number ( $s$ ), with its possible values of  $+\frac{1}{2}$  and  $-\frac{1}{2}$ , is retained in the molecular notation.

Apart from the introduction of the  $\lambda$  value an electron is represented in a manner analogous to that used for atoms: thus a  $2p\sigma$  electron, means that  $n = 2$ ,  $l = 1$  and  $\lambda = 0$ ; the number of such electrons, *e.g.*, two, would be indicated by a suffix, thus  $2p\sigma^2$ . An alternative type of representation more suited for an actual molecule than for those approaching the united atom state is considered later (p. 79). According to the Pauli principle, no two electrons can have the same values of  $n, l$  and  $\lambda$ , unless their spins are opposed; it follows, therefore, that there can be only two equivalent  $\sigma$  electrons, with spins  $+\frac{1}{2}$  and  $-\frac{1}{2}$ , but four equivalent  $\pi$  electrons are possible, thus  $\lambda = \pm 1$ ,  $s = \pm \frac{1}{2}$ ; similarly a maximum of four  $\delta$  electrons can be found in one group.

**Term Formulæ for Diatomic Molecules.** The representation of molecular terms is very similar to that already described for atoms, except that the Greek letter  $\Lambda$  replaces  $L$  and the term symbols,  $\Sigma, \Pi, \Delta$  are used for  $\Lambda = 0, 1, 2$ , respectively; the possible values of  $\Lambda$  are given by the sum of the  $\lambda$  values, the signs being included. The term symbol is preceded by the multiplicity  $2S + 1$  as superscript, and is generally followed by the sum of  $\Lambda + \Sigma$  as a subscript, where  $\Sigma$  is related to  $S$ . If the molecule consists of completed groups only, as for example carbon monoxide, which has the electron configuration  $1s\sigma^2 2p\sigma^2 3p\sigma^2 2p\pi^4 3d\sigma^2$ , then  $\Lambda = 0$  and  $S = 0$ , and the term formula is  $^1\Sigma$ ; most stable diatomic molecules are of this type. When there is one  $\sigma$  electron apart from completed groups, the value of  $\Lambda$  must be 0 and  $S$  is  $\frac{1}{2}$ , so that the molecule is in a  $^2\Sigma$  state. Similarly it can be shown that either one or three  $\pi$  electrons, in the same group,



give  ${}^2\Pi$  states. When there are two equivalent  $\pi$  electrons in the molecule three different states are possible; the values of  $\lambda$  must be  $+1$  or  $-1$ , and so  $\Lambda$  is 2 or 0, according as  $\lambda$  is the same or different for the two electrons. The corresponding term symbols are  $\Delta$  and  $\Sigma$ , respectively. In the former case  $n$ ,  $l$  and  $\lambda$  are the same for the pair of electrons, and so the spins must be anti-parallel, that is  $+\frac{1}{2}$  and  $-\frac{1}{2}$ , by the Pauli principle; hence  $S = 0$ , and the state is  ${}^1\Delta$ . On the other hand, when the  $\lambda$  values are different the electron spins can be either anti-parallel, when the state is  ${}^1\Sigma$ , or parallel, when  $S = 1$ , and the state is  ${}^3\Sigma$ . These considerations are important in connection with the electronic structure of the oxygen molecule (p. 83). Other factors have frequently to be specified in order to characterise the state of a molecule; these are important for spectroscopic and other purposes, but are too complicated to be discussed in this book (see also "Recent Advances in General Chemistry," Chapters II. and III.).

### THE ELECTRONIC THEORY OF VALENCY

**Kossel's Theory.** Although various authors, particularly J. J. Thomson (1904), had realised that there was some connection between the extra-nuclear electrons and the valency of an element, the first definite ideas leading up to the modern electronic theory of valency must be attributed to Kossel (1916), and to G. N. Lewis (1916) independently. Both these authors emphasised the fact that the electronic arrangements to be found in the inert gases (Group O) were the most stable structures, and that other atoms in chemical combination tried to attain the inert gas structure. Kossel considered a group of five elements, two on each side of an inert gas, thus :—

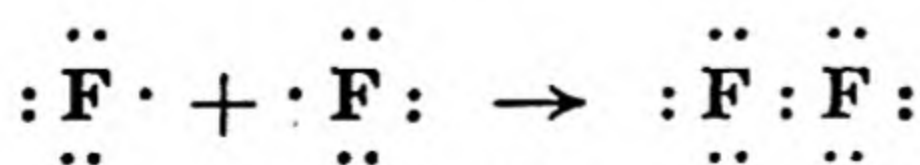
Element . . . . .	O	F	Ne	Na	Mg
Extra-nuclear Electrons	8	9	10	11	12
Valency . . . . .	-2	-1	0	+1	+2

With ten electrons a stable arrangement results, and this can be attained if an oxygen atom gains two electrons, or fluorine one electron; sodium and magnesium, on the other hand, can attain



the stable arrangement by losing one and two electrons, respectively. It is clear, therefore, that oxygen will tend to gain two electrons, and so form a bivalent negative ion, whereas fluorine will try to gain one electron, and so readily form a univalent negative ion; sodium and magnesium, on the other hand, will tend to lose electrons, and so form positive univalent and bivalent ions, respectively. In the combination of an electronegative with an electropositive element, *e.g.*, fluorine and sodium, the former can take up the electron which the latter is prepared to yield, and so a stable sodium fluoride will result. The same mechanism can account for the structure of salts in general: the positive and negative ions being held together by electrostatic forces. According to Kossel, therefore, the valency of an element was regarded as the number of electrons it must lose, if electropositive, or gain, if electronegative, in order to attain the same electronic structure as an inert gas.

**Lewis' Theory and the Electron Octet.** This theory may account satisfactorily for the valencies of the elements which are close to an inert gas in the periodic classification, but it can hardly account for others further away. According to Kossel, nitrogen should tend to form an  $N^{3-}$  ion, but this does not seem very probable. Further, in the long periods of the classification an element may be nine electrons short of the inert gas structure, and the chances that this number of electrons will be gained or lost are very remote. In G. N. Lewis' theory, however, the type of combination postulated by Kossel was restricted to ionised compounds, *e.g.*, salts, and in addition it was suggested that two atoms could *share* electrons in the attempt of each to attain the inert gas structure, the shared electrons counting towards both atoms. For example, fluorine has nine electrons, of which two may be regarded as forming the first stable group, leaving seven in the second group, where eight are required for complete stability. If two fluorine atoms share one pair of the second shell of electrons between them, thus \*



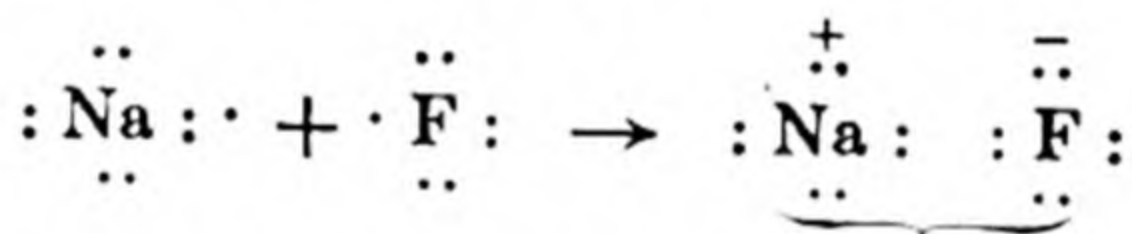
\* The symbol of an element is used to represent the nucleus and all the inner electron shells; thus F represents the fluorine nucleus and two electrons.



each completes the group of eight electrons required, and a fluorine molecule results. It is to be noted that in this type of combination ions are not produced. The completion of the outer layer of eight electrons, or "electron octet," was considered to be the aim of all elements in chemical combination, and by sharing electrons between them atoms are able to complete their "octets" with a smaller number than would be required by the Kossel method of union. The Lewis method of combination, therefore, makes it possible for two or more elements which are short of electrons, namely electronegative elements, *e.g.*, oxygen and nitrogen, to combine together; in these cases ions do not result.

### ELECTROVALENCY AND COVALENCY

**Electrovalency.** It is clear that at least two types of chemical combination are possible; the first involves the passage of an electron from one element to the other, *e.g.*, sodium with nine *outer* electrons, and fluorine with seven, thus

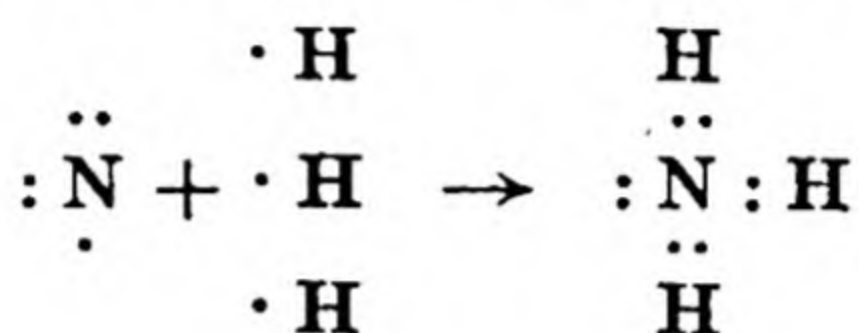


leading to the production of a positive sodium ion and a negative fluorine ion held together by electrostatic forces. Langmuir, in his development of the electronic theory of chemical combination, called this "electrovalency"; it is found in general when an electropositive element, or radical, unites with an electronegative element, or radical, and an electrolyte results.

**Covalency.** The second type of chemical combination, called by Langmuir "covalency," results when electrons are shared between two elements; the elements involved are generally, although not always, electronegative and the linkages are non-ionisable. This type of combination is very common in organic compounds. Lewis made it quite clear that the sharing of electrons can only occur in *pairs*; as evidence for this he quoted the fact that with only very few exceptions, *e.g.*, nitric oxide, nitrogen dioxide, chlorine dioxide and indium dichloride, chemical compounds contain an *even* number of electrons. The

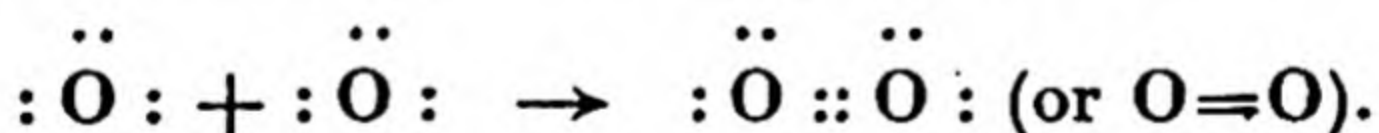


pair of electrons, shared between two atoms, is the equivalent of the ordinary valency bond, and the number of shared pairs, or duplets, gives the valency of the atom. For example, nitrogen with seven electrons has five in the outer shell, and so requires three more to complete its octet; the hydrogen atom has one electron only, but would prefer to possess two in order to have the same electronic structure as the stable atom helium. Each hydrogen atom gives one electron and the nitrogen atom three electrons towards the sharing of three pairs, thus



so that in the molecule of ammonia each of the constituent atoms has a stable electronic arrangement. Since the nitrogen atom has three shared duplets its valency may be regarded as three.

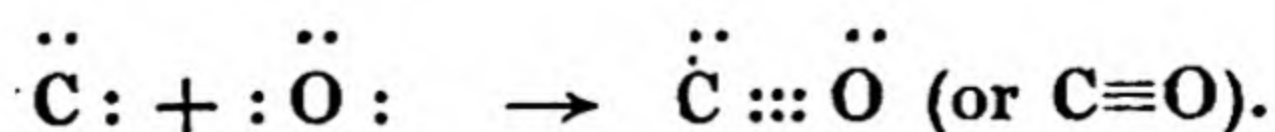
When two atoms are attached by a double bond it is supposed that they share four electrons, *i.e.*, two pairs, between them; in this way it may be possible for two atoms possessing only a total of twelve electrons in their outer shells to complete both their octets. This probably occurs when two oxygen atoms unite in the oxygen molecule (see, however, p. 83), thus



In the same way a triple bond implies the sharing of three pairs, *i.e.*, six electrons, so that the two atoms concerned may complete their octets when they together possess only ten electrons in their outer shells. This type of linkage is probably found in the nitrogen molecule



and in carbon monoxide

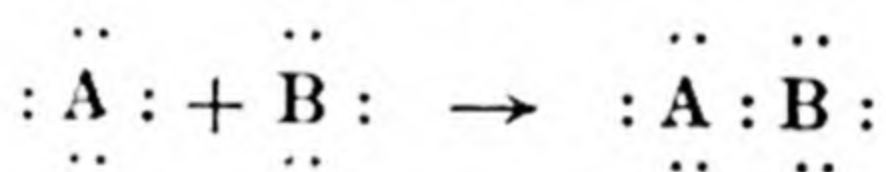


The curious fact is to be noted that in the latter compound both atoms appear to be tervalent; this apparent anomaly will be



explained subsequently. In order that two atoms may be joined together by a "quadruple" bond it would be necessary for the eight electrons to be in one plane; such an arrangement appears to be impossible, and no example of the linkage is known. This probably accounts for the fact that carbon is unable ordinarily to form a simple molecule  $C_2$ , or  $C \equiv C$ , but can only acquire stability by building up complex structures such as are found in diamond and graphite.

**Semi-Polar Bonds.** Before proceeding to discuss in detail the properties of compounds involving the two types of valency, mention must be made of a special type of covalency which results when *both* of the shared electrons forming a single linkage are supplied by only one of the two atoms concerned. An example of this type of union (Lowry, 1923) would be



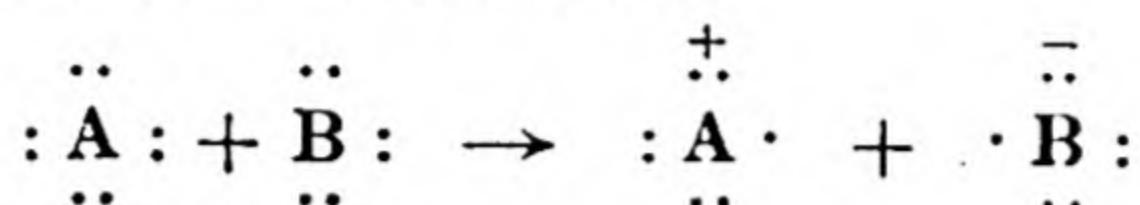
where both electrons of the shared duplet are supplied by the molecule  $A^*$ ; the latter is called the "donor" and  $B$  is the "acceptor." It will be noted that  $A$  originally possessed  $n + 8$  electrons and  $B$  had  $n' + 6$ , where  $n$  and  $n'$  are the numbers in the inner sheaths; if  $A$  and  $B$  were originally neutral these also represent the net positive charges on the nuclei. In the compound  $AB$ , however, the number of electrons associated with  $A$  is now  $n + 7$  and with  $B$  it is  $n' + 7$ , the shared duplet counting as one electron to each atom; it follows, therefore, that  $A$  now has a net positive charge, and  $B$  a net negative charge. A compound containing this type of covalency will consequently be "polar"; that is the molecule as a whole is neutral, but the centres of "gravity" of the positive and negative charges do not coincide (see Chapter III.). Since the two portions of the molecule are held together by a pair of electrons they will not separate in order to form ions; the name "semi-polar" bond is given to this type of linkage, and molecules in which it is present always contain an electrical "dipole" (see Chapter III.). The title of "dative"

\*  $: \ddot{A} :$  is *not* an atom, but a molecule or ion with octets complete; otherwise it would represent an inert gas.

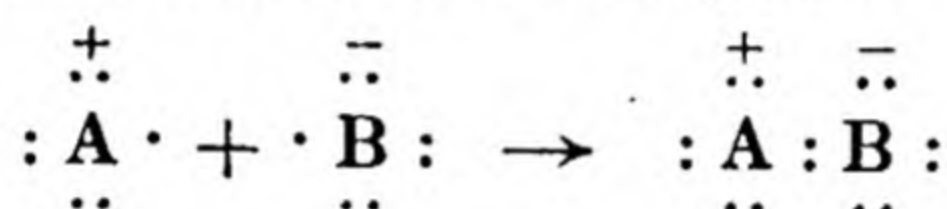


bond, which has much to recommend it, has been proposed by Menzies (1928) and is frequently to be found in the literature; it is in harmony with the view that one atom gives both electrons forming the bond.

The formation of the "semi-polar" bond can be examined from another point of view: it may be imagined that an electron is first transferred from A to B, thus



yielding  $\overset{+}{\text{A}}$  and  $\overset{-}{\text{B}}$ . The resulting ions have each a "lone" electron, and each can consequently acquire greater stability by sharing this with the other in a covalent bond, thus



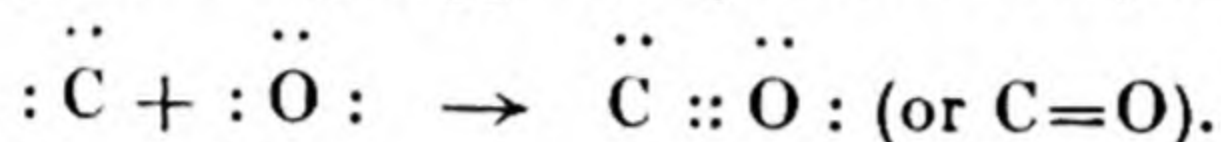
The semi-polar covalency thus implies a combination of one electrovalency and one covalency, and so has been called a "mixed double bond" (Lowry, 1923) or "semi-polar double bond" (Sugden, 1925). There are various ways of representing

this type of linkage; one method is  $\overset{+}{\text{A}}-\overset{-}{\text{B}}$ , which indicates the duplex nature of the bond, and another is to use an arrow with the head pointing in the direction in which the pair of electrons has been transferred, thus  $\text{A} \rightarrow \text{B}$ . Both methods of representation have many advantages and a few disadvantages, and both are to be found in current chemical literature; in this book the arrow will be used, in general, when two molecular species, each capable of separate existence, are united together. The arrow in such instances indicates the transfer of a pair of electrons and so represents the process by means of which the final compound is probably formed. It will be seen subsequently that Werner's co-ordination valency, which was regarded as being responsible for the union of two substances each capable of separate stable existence, *e.g.*,  $\text{CrCl}_3$  and  $\text{NH}_3$ , is a type of semi-polar bond, and it is for this type especially that the arrow will be used. Sidgwick applies the term "co-ordination valency" to all types of semi-polar linkages, and always represents it by an arrow; it would be

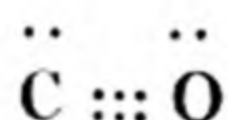


more in keeping with Werner's original concepts, however, to use the expression in the restricted sense suggested here. As this book is intended to be a guide to the literature of physical chemistry an attempt will be made to strike a mean between the possible alternatives.

In the formation of a molecule of carbon monoxide it may be supposed that the first possibility is the sharing of two pairs of electrons, one pair being supplied by each atom, thus



In the resulting doubly-linked molecule, however, the octet of the carbon atom is not complete, although it could become so if another pair of electrons, *supplied entirely by the oxygen atom*, were shared, thus



The linkages involved are two ordinary covalencies and one co-ordinate valency, and the formula should be written  $\bar{\text{C}} \equiv \overset{+}{\text{O}}$  or  $\text{C} \equiv \text{O}$ . Such a structure, at first sight, appears to imply tervalent carbon, but since a semi-polar bond is the equivalent of a double bond the atom remains quadrivalent, in the classical sense; this aspect of the matter has, however, little significance. In the same way the oxygen may be regarded as bivalent, as it supplies only two electrons in the shared duplets. Other aspects of the structure of carbon monoxide will be considered later (see p. 91).

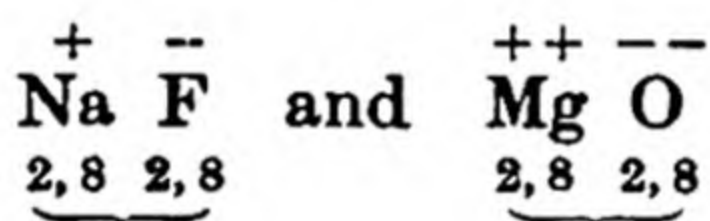
### ELECTROVALENCY

When two atoms or groups are joined together by an electrovalency, no electrons are shared, but the two portions of the molecule, actually oppositely charged ions, are supposed to be held together by electrostatic forces only, and not by a definite bond. In a crystal of an electrovalent compound, *e.g.*, sodium chloride, the molecule would not be expected to be the unit of the crystal structure; it is more probable that there should be separate lattices of sodium ions and of chlorine ions. The work of W. H. and W. L. Bragg, using the X-ray diffraction method, has

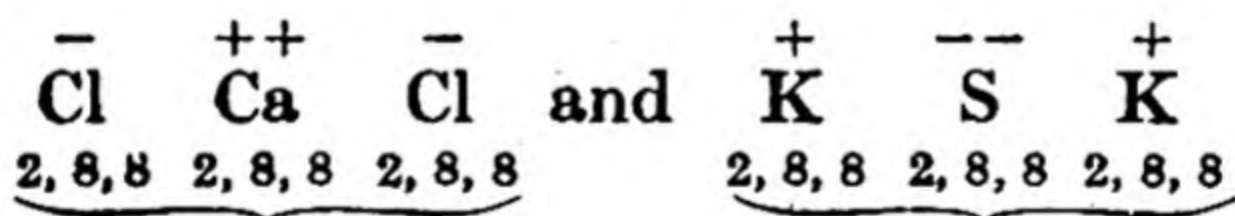


shown that salt crystals are in fact made up of two such interpenetrating lattices. It was considered at one time that there was evidence to show that the units in the lattice were ions and not merely atoms, but this fact, although probable, cannot be regarded as established experimentally. The main conclusion, is, however, that the molecule of sodium chloride containing an atom of sodium *definitely linked* to an atom of chlorine does not exist in the crystal; this result complies with anticipations from the electronic theory of valency.

Langmuir (1919) has pointed out that the theory of ionic structure, resulting from the concept of electrovalency, accounts for the existence of the isomorphous sodium fluoride and magnesium oxide, and calcium chloride and potassium sulphide. On the basis of Mitscherlich's law this isomorphism is certainly anomalous, but if the electron shells of the *ions* constituting the different compounds are examined the resemblance is marked. The structures of sodium fluoride and magnesium oxide, for example, are



and those of calcium chloride and potassium sulphide are



If isomorphism depends on a similarity of electron shells the electrovalent structures of the compounds under discussion readily account for the observed facts; the similarity in the structures would not be observed however unless the substances were assumed to have *ionic* structures involving electrovalencies.\*

**Electrolytic Conductance.** If a crystal of an electrovalent compound consists of ions, it is reasonable to suppose that when this substance is dissolved in a suitable solvent, or else heated until it melts, the restraining forces of the crystal lattice are no

\* More striking examples of apparently anomalous isomorphism are those recently observed of the berylliofluoride ion ( $\text{BeF}_4^-$ ) and the fluophosphate ion ( $\text{PO}_3\text{F}^-$ ) with the sulphate ion ( $\text{SO}_4^{--}$ ); these cases are readily understood from a consideration of the electronic arrangements of the ions concerned.

UNIVERSITY OF TORONTO LIBRARY  
6389



longer present, and so the ions should be able to move under the influence of an electrical field. Such solutions, or melts, should thus be good conductors of electricity, whereas compounds not containing an electrovalent link should give non-conducting, or very poorly conducting, liquids. Biltz and Klemm (1926) have made a compilation of the electrical conductances of a number of fused chlorides just above their melting points; since the temperatures were widely different the results are not exactly comparable, but they are sufficiently definite to establish certain facts. The main results are given in Table III.; as a rule the equivalent conductances are stated, but in some cases the specific conductance ( $\kappa$ ) is given.

TABLE III.—*Conductances of Fused Chlorides at their Melting Points*

Group I.	II	III.	IV.	V.	VI.
HCl < $10^{-6}$					
LiCl 166	BeCl <sub>2</sub> < 0.086	BCl <sub>3</sub> 0	CCl <sub>4</sub> 0		
NaCl 133	MgCl <sub>2</sub> 28.8	AlCl <sub>3</sub> $1.5 \times 10^{-5}$	SiCl <sub>4</sub> 0	PCl <sub>5</sub> 0	
KCl 103	CaCl <sub>2</sub> 51.9	ScCl <sub>3</sub> 15	TiCl <sub>4</sub> 0	VCl <sub>4</sub> 0	
RbCl 78.2	SrCl <sub>2</sub> 55.7	YCl <sub>3</sub> 9.5	ZrCl <sub>4</sub> —	NbCl <sub>5</sub> $\kappa = 2 \times 10^{-7}$	MoCl <sub>5</sub> $\kappa = 1.8 \times 10^{-6}$
CsCl 66.7	BaCl <sub>2</sub> 64.6	LaCl <sub>3</sub> 29	HfCl <sub>4</sub> —	TaCl <sub>5</sub> $\kappa = 3 \times 10^{-7}$	WCl <sub>6</sub> $\kappa = 2 \times 10^{-6}$
			ThCl <sub>4</sub> 16		UCl <sub>4</sub> $\kappa = 0.34$

Although the varying mobilities of the cations may account for some portion of the variation in electrical conductance, there is no doubt that the chlorides can be divided into two distinct groups by the stepped line in Table III., one of which contains the good conducting chlorides and the other the almost non-conducting type. In other words, the line makes a demarcation between compounds containing chlorine attached by an electrovalency, and those in which the chlorine is joined by a definite covalent bond.

Apart from hydrogen chloride, which will be discussed later, the



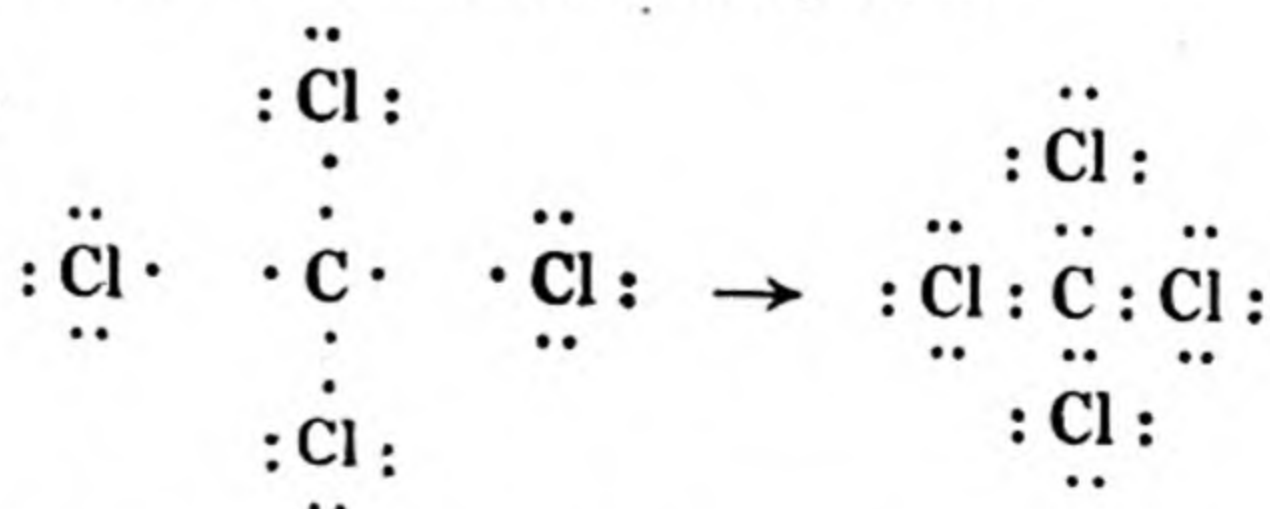
chlorides of Group I. are all good conductors, so that there is no doubt of the presence of an electrovalency in these compounds. In this group the elements require to lose one electron only in order to acquire stable structures, and hence in chemical combination there will be a strong tendency for the transfer to occur, and an electrovalency to result. At first sight it would be expected that these elements could never form covalencies, since seven electrons would need to be gained; it will be seen later, however, that covalent compounds of the alkali metals do exist.

**The Fajans Theory.** In Group II. beryllium chloride is a poor conductor, although the other members of this series form good conducting melts. It appears that in the first element of the group the linkage is mainly covalent and not electrovalent. This apparent anomaly is well accounted for by the important but simple theory developed by Fajans (1924). In a molecule consisting of two ions the electrostatic attraction holding the ions together will tend to draw them closer, with the result that the "orbits" (or fields) of the outer electrons become distorted or deformed. If this attraction becomes sufficiently great the distortion will be so considerable that some of the electrons instead of being associated with one of the ions will be shared between both; that is to say, the electrovalency tends to pass over into a covalency when the attraction between the ions is large. The greater the charge on the cation and on the anion the greater will be this deformation, and so ions of high valency, whether positive or negative, favour the formation of covalent, rather than electrovalent, linkages. Further, the smaller the radius of the positive ion the greater will be the electrostatic field in its vicinity, and so the more will this ion distort the electrons of the anion. In the same way the larger the anion the less strongly can it hold its outermost electrons, and hence the more readily can their "orbits" become distorted. An electrovalency will consequently tend to pass into a covalency when the cation is small and the anion large. Beryllium forms a small ion, and one that has two charges, and so it is not very surprising that in the fused chloride the linkage is mainly covalent; the small measured conductance shows, however, that there is some ionisation. In a solvent of high



dielectric constant the electrostatic forces between the ions will be considerably diminished, and the tendency for an electrovalency to become a covalency will consequently not be so marked. In accordance with this view it is found that a solution of beryllium chloride in water, although hydrolysed to some extent, is quite a good conductor. It is clear, therefore, that beryllium, as might be anticipated, does form an electrovalent linkage with chlorine, but this tends to become a covalent bond unless the force of electrostatic attraction is in some way diminished.

The theory of Fajans accounts in a very simple manner for the stepped line dividing electrovalent from covalent halides; the higher the valency of a cation the larger must it be in order that it may retain its electrovalency. In Group III. the definite ionic structure apparently commences with scandium, but aluminium chloride, like beryllium chloride, forms a conducting solution in water. Boron trichloride, however, gives no indication of the presence of an electrovalency under any known conditions; it must be assumed, therefore, that the boron atom always shares three electron pairs with the three chlorine atoms forming a group of six electrons. This sextet is apparently stable, and is more readily formed than a trebly charged boron ion. In the fourth group the position of the dividing line is inferred from other properties of the halides; the conductances in the fused state cannot all be determined on account of sublimation of the solids. Since the carbon atom has four electrons in the outer shell it can acquire a stable electronic arrangement either by gaining four electrons, or by losing the same number; it is clear that owing to the smallness of the carbon atom it is much easier for it to gain electrons than to lose them and become an ion. In carbon tetrachloride four covalencies are involved, thus



and there is no tendency at all to form electrovalencies.



If an element forms two ions of different valencies then the Fajans rules would imply that the tendency of its compounds, *e.g.*, halides, to ionise will be greatest when the charge, that is valency, is least. The results for the equivalent conductances at the melting points of various halides in Table IV. confirm this view.

TABLE IV.—*Conductances at the Melting Point of Halides of Differing Valency*

Hg <sub>2</sub> Cl <sub>2</sub>	circa 40	InCl	130	TlCl	46.5	SnCl <sub>2</sub>	21.9
HgCl <sub>2</sub>	$2.5 \times 10^{-3}$	InCl <sub>2</sub>	29	TlCl <sub>3</sub>	$< 2.5 \times 10^{-4}$	SnCl <sub>4</sub>	0
		InCl <sub>3</sub>	15				

It may be argued that mercury is not really univalent in mercurous chloride, but as the net charge of two units is spread over two atoms this means a unit charge per atom which, from the Fajans standpoint, is equivalent to univalency.

**Boiling Points.** Since compounds containing an electrovalency depend for their existence on electrostatic forces it is very probable that such compounds possess strong external fields of force. The ions in the crystal lattice exert a powerful attraction for one another, so that a considerable amount of work must be done in order to separate them. It is natural to suppose, therefore, that electrovalent compounds will have high melting and boiling

TABLE V.—*Boiling Points of Halides at 1 Atmosphere Pressure*

Group I.	II.	III.	IV.	V.	VI.
LiCl 1350°	BeCl <sub>2</sub> ca. 550°	BCl <sub>3</sub> 18°	CCl <sub>4</sub> 78°		
NaCl 1470°	MgCl <sub>2</sub> 1412°	AlCl <sub>3</sub> 183°	SiCl <sub>4</sub> 58°	PCl <sub>5</sub>	
KCl 1500°	CaCl <sub>2</sub> > 1600°	ScCl <sub>3</sub> > 1000°	TiCl <sub>4</sub> 136°	VF <sub>5</sub> 111°	
RbCl 1400°	SrCl <sub>2</sub> —	YCl <sub>3</sub> —	ZrCl <sub>4</sub> Sublimes	NbCl <sub>5</sub> 241°	MoCl <sub>5</sub> [ MoF <sub>6</sub> ] 268° [ 35° ]
CsCl 1270°	BaCl <sub>2</sub> —	LaCl <sub>3</sub> > 1000°	HfCl <sub>4</sub> Sublimes	TaCl <sub>5</sub> 242°	WCl <sub>6</sub> [ WF <sub>6</sub> ] 346° [ 19° ]
			ThCl <sub>4</sub> 922°	—	[ UF <sub>6</sub> ] [ 56.2° ]



points, whereas with covalent compounds these will be much lower. Paneth (1920) has shown that the hydrides of the elements can be divided into two groups : those which are good conductors having very high boiling points, and the non-conductors which are readily volatile. The same distinction is to be found, although perhaps not so markedly, with the chlorides, the approximate boiling points for which are given in Table V.; the parallelism with the conductances in Table III. is quite clear.

The influence of valency is brought out in the comparison of the boiling points of the two halides of tin, and of the three halides of titanium, thus :

$\text{SnCl}_2$	606°	$\text{TiCl}_2$	Very high.
$\text{SnCl}_4$	114°	$\text{TiCl}_3$	„ „
		$\text{TiCl}_4$	135°

Stannous chloride is definitely a salt and contains an electrovalency, whereas the stannic compound is like a typical chloride of a non-metal in which covalencies only are concerned. Of the three titanium chlorides the first two mentioned are, like most salts, insoluble in ether, whereas the tetrachloride is soluble in that liquid, indicating the presence of covalent links.

The melting point, like the boiling point, is often used as a criterion of the type of valency present in the compound ; Pauling (1932) considers, however, that the conclusions may be misleading. The melting points of aluminium fluoride and silicon fluoride are 1040° and — 77° respectively, but this is not regarded as denoting a change from electrovalency to covalency. It is suggested that since the co-ordination number of aluminium (6) is greater than the number of atoms of fluorine attached to an atom of the metal in the fluoride, each fluorine atom in the crystal is shared between two or more atoms of aluminium, so that there is a high degree of cohesion and the melting point is consequently high. In silicon tetrafluoride, however, the co-ordination number (4) is equal to the number of fluorine atoms to each atom of silicon, and so the crystals consist of discrete molecules  $\text{SiF}_4$ , held loosely together ; the substance, therefore, melts and boils at low temperatures. This factor may explain why beryllium chloride has a high boil-

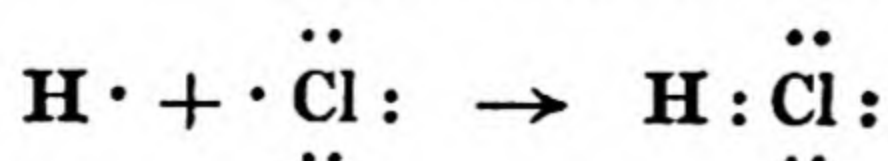


ing point (Table V.), although its melt is almost non-conducting (Table III.).

**Solubility.** Characteristic of electrovalent compounds is their solubility in associated solvents, particularly those containing a hydroxyl group, *e.g.*, water or an alcohol; covalent compounds are generally sparingly soluble in water, but are soluble in non-associated organic liquids. Most salts are known generally to be insoluble in the usual organic solvents, but where there is a tendency for an electrovalency to become a covalency as a result of the presence of a small or highly charged cation, or a large anion, or both, the solubility becomes marked. Although the alkali halides represent very definite electrovalent compounds there is, in harmony with Fajans' theory, some inclination for a covalent link to form with the smallest ion lithium. The halides of this element are all soluble in ethyl acetate, a typical non-associated solvent; when the anion is large, as in the iodide and perchlorate, the solubility is quite considerable. The solubility of silver perchlorate in benzene is, however, not so easy to understand.

### THE DUALITY OF HYDROGEN

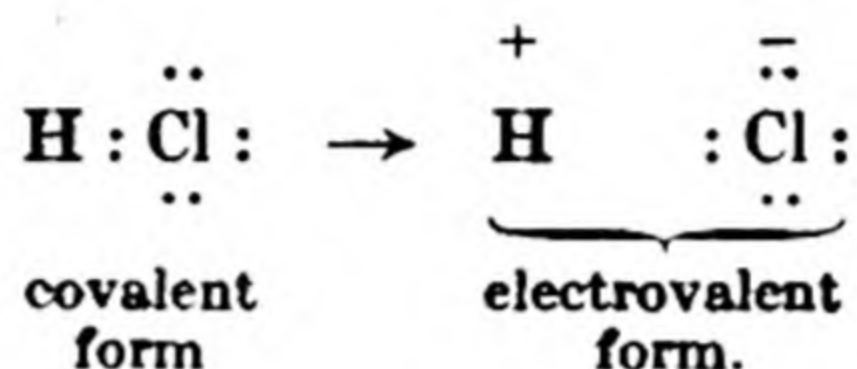
The element hydrogen presents an extreme case of the applicability of the Fajans distortion theory; since the hydrogen ion is very much smaller than any other ion the tendency for an electrovalency to become a covalent link should be very marked. This tendency is favoured by the fact that hydrogen can attain a stable electronic arrangement not only by losing an electron, and so becoming a positively charged hydrogen ion (or proton,  $H^+$ ), but also by gaining one electron, and so attaining the two required to complete the first sheath of electrons; these two electrons can then be shared as a covalency with another atom. In hydrogen chloride, for example, each atom contributes an electron towards the formation of a duplet which is then shared by both, thus



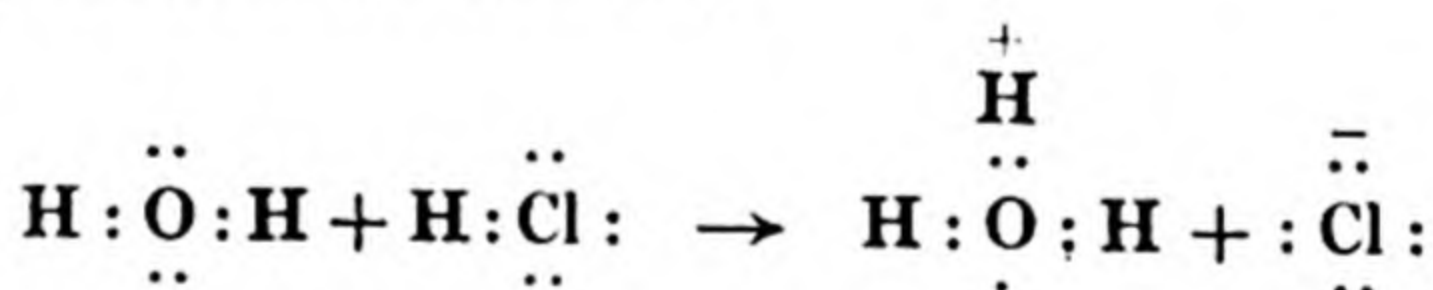
According to this view hydrogen chloride is a covalent compound, and should have a low boiling point and be a non-conductor;



this is borne out by actual fact (Table III.), although the molecule is definitely polar (see p. 154). A solution in a suitable solvent, *e.g.*, water, is an excellent conductor, and so presumably the covalency has become an electrovalency; this could occur simply as a result of the shared duplet being associated more with the chlorine atom, thus



The ionisation of hydrogen chloride, and probably of all other acids, is not merely a question of the dielectric constant of the medium being sufficient to decrease the electrostatic forces in the molecule, since it is very probable that the "bare" hydrogen ion, or proton, cannot be formed at all readily (see p. 468), but can only exist in solution in a solvated form, *e.g.*,  $\overset{+}{\text{H}}(\text{H}_2\text{O})$ , or  $\text{H}_3\text{O}^+$ . Ionisation of an acid results, therefore, when the solvent is a better proton attractor than is the anion of the acid, and the process may be represented electronically

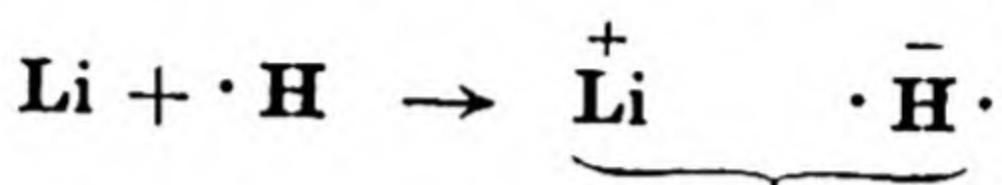


The same relationship may be regarded as applying to other acids; they can all have quite stable structures either as covalent molecules, or else in the ionised form, and the extent of ionisation depends on the nature of the anion and of the solvent. In a proton-attracting solvent the ionisation will be considerable and the acid is a strong one, but it will be weak in a solvent to the molecules of which a proton cannot readily attach itself. The strength of an acid will also be greater the more the proton repelling, or electron attracting, tendency of the anion residue (see p. 468). The importance of the two factors, anion and solvent, in determining the strength of an acid is shown by the observation that although hydrogen chloride produces a strong acid solution both in water



and in alcohol, nitric acid is a weak acid in the latter solvent (Hartley, 1929).

**Negative Hydrogen.** An interesting aspect of the theory that hydrogen can be stable either with no electrons ( $\text{H}^+$ ) or with a pair of electrons ( $\text{H}^-$ ), led G. N. Lewis (1916) to suggest that metal hydrides involved an electrovalent union, for example



Such compounds should be good conductors, as has already been mentioned, and on electrolysis hydrogen should be evolved at the *anode*. In 1922 Bardwell electrolysed a solution of calcium hydride in a eutectic mixture of potassium and lithium chlorides; hydrogen was liberated at the anode in the amount required by Faraday's laws of electrolysis, but no gas was set free at the cathode. Although the conclusions drawn from this experiment have been criticised by Bancroft, it seems very probable that it does yield evidence in favour of the existence of the negatively charged hydrogen ion.

## COVALENCY

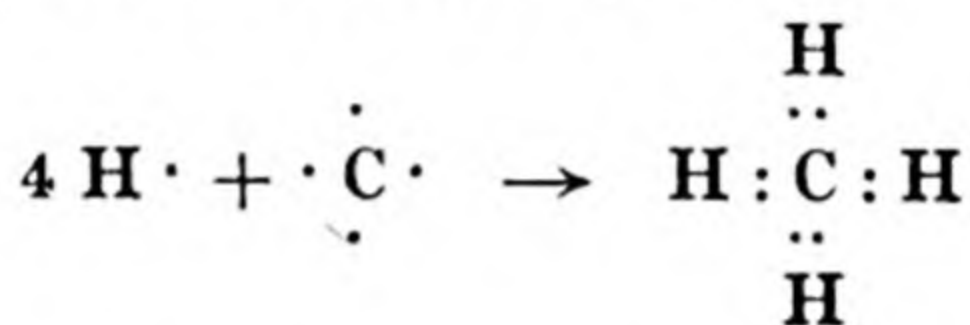
**Directional Valencies.** Covalent compounds, as already implied, are readily volatile non-conductors, and usually consist of electro-negative elements; they are generally soluble in non-associated solvents with low dielectric constants. The presence of a covalent linkage resulting from the sharing of electrons implies a definite *directional* bond, so that stereo-isomerism is possible; this type of isomerism never occurs in purely electrovalent compounds, since the union in such cases is non-directional, and merely a general electrostatic attraction. Stereo-isomerism has been observed in compounds containing electrovalencies (Werner), but it is the covalencies in the molecule which are responsible.

It is well established that in the carbon atom the covalency bonds are directed towards the corners of a regular tetrahedron; such an arrangement may readily be correlated with the formation of a stable electron octet. Although there is no certainty as to the nature of the electron it may be supposed that in the octet of an

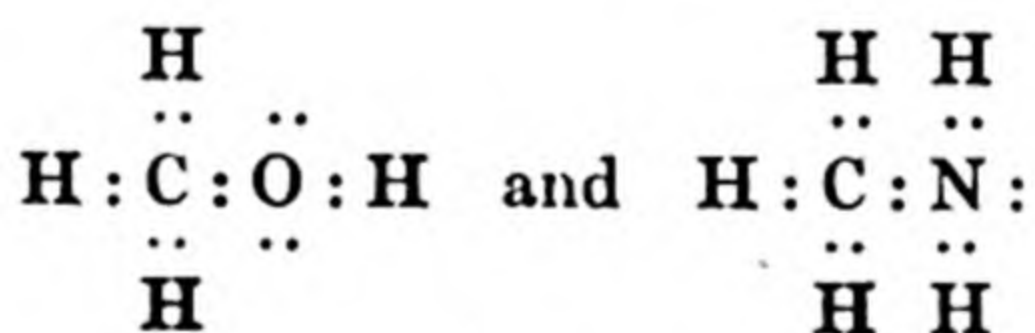


inert gas the points corresponding to the electrical centres of the electrons will be uniformly distributed on a sphere. If the electrons are shared in pairs, however, this arrangement is distorted, and a uniform distribution of four pairs corresponds exactly to the corners of a regular tetrahedron. Hence it may be supposed at first sight that in any complete octet the valency bonds are similar in direction to those in the carbon atom; the matter is not quite so simple as this line of argument would imply. The subject must be left for the present, however, until the treatment based on wave mechanics can be discussed (p. 70).

In carbon and nitrogen compounds the covalency is, of course, very common; in methane, for example, the four hydrogen atoms each contribute an electron, and the carbon atom four electrons, towards the formation of four pairs, thus

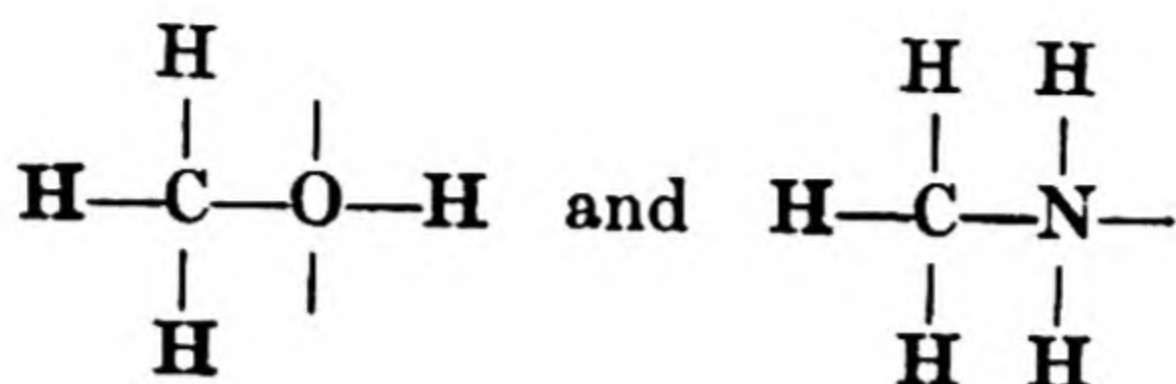


The carbon has a complete octet and each hydrogen a duplet, and so a stable molecule results. Other examples of a slightly more complex type are found in methyl alcohol and methylamine, which are



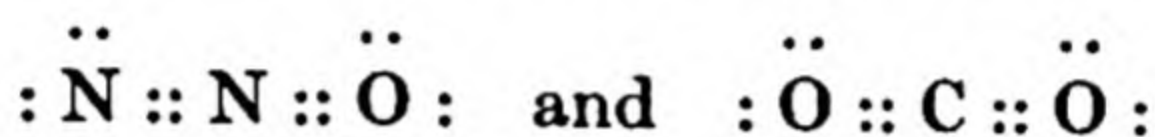
respectively, each atom having its requisite stable electronic arrangement. In general, for organic compounds the electronic formulæ are very similar to the ordinary chemical formulæ: a pair of shared electrons representing every single linkage, two pairs for a double linkage, and six shared electrons for a triple bond. Reference will be made subsequently to the modification necessary when a semi-polar bond is present. The electronic formulæ have the advantage of showing the *unshared* pairs, sometimes called "lone pairs," of electrons, as for example in the formulæ given above for methyl alcohol and for methyl-

amine; the ordinary representation is modified by some authors, thus



where every line represents a pair of electrons, the oxygen having two and the nitrogen one unshared pair.

**Isosteres.** An interesting consequence of the electronic theory of valency has been mentioned by Langmuir (1919); the structures of nitrous oxide and carbon dioxide may be written



and the nuclear charges for the atoms are 7, 7, 8 and 8, 6, 8 respectively. There is thus a definite similarity between the two compounds which had not previously been expected; this resemblance was found to apply also in a most striking manner to their physical properties, as the results in Table VI. indicate.

TABLE VI.—*Comparison of Physical Properties of Nitrous Oxide and Carbon Dioxide*

	Nitrous Oxide.	Carbon Dioxide.
Critical pressure (atm.) . . .	75	77
Critical temperature (° C.) . . .	35.4	31.9
Viscosity at 20° . . .	$148 \times 10^{-6}$	$148 \times 10^{-6}$
Density of liquid at 10° . . .	0.856	0.858
Refractive index, D line at 16° . . .	1.193	1.190
Dielectric constant of liquid at 0° . . .	1.598	1.582
Magnetic susceptibility . . .	$0.12 \times 10^{-6}$	$0.12 \times 10^{-6}$
Solubility in water at 0° . . .	1.305	1.708
Solubility in alcohol at 15° . . .	3.25	3.18

Langmuir calls such pairs of compounds with similar electronic structures "isosteres," examples being nitrous oxide and carbon dioxide, and nitrogen and carbon monoxide.



It is interesting to note too that the molecular weights are identical, and the calculated parachors (Chapter II.) almost so ; the surface tensions of the liquids must, therefore, be very similar.

**The Octet not a Maximum.** It has been assumed hitherto that the maximum number in a group of valency electrons is the eight forming an octet ; there is reason to believe, however, that this number can be exceeded. For example, sulphur forms a hexafluoride,  $\text{SF}_6$ , which is a very stable compound ; it is a gas which is unacted upon by sodium below red heat and is not decomposed by hot alkaline solutions. From its ready volatility it follows that sulphur hexafluoride is a covalent compound, and since two fluorine atoms have not been found attached together, except in the fluorine molecule, it appears that each of the six atoms is joined directly to the central sulphur atom. The latter had originally six valency electrons, and if these are all contributed towards shared duplets the six fluorine atoms are enabled to complete their octets ; the sulphur atom would then be surrounded by a group of *twelve* electrons.

### SINGLE ELECTRON LINKAGES

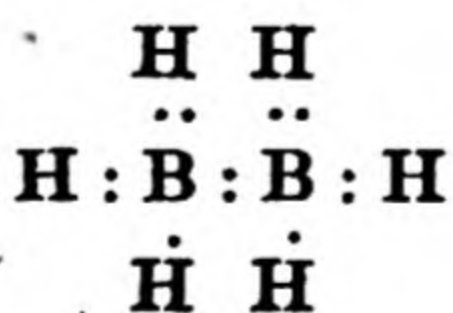
Many investigators (*e.g.*, Sidgwick, G. N. Lewis) consider that an increase of the valency group to twelve, and even to sixteen as in osmium octofluoride,  $\text{OsF}_8$ , is not impossible. Sugden, however, mainly as a result of his work on the parachor (Chapter II., p. 116), has concluded that the electron octet involved in valency bonds cannot be exceeded ; he accounts for the formation of compounds like phosphorus pentachloride and sulphur hexafluoride by assuming that some or all of the halogen atoms are joined to the central atom by linkages involving the sharing of a *single electron* instead of a pair. These bonds are called by Sugden "singlet," or "odd electron," linkages. According to this theory the central atom in phosphorus pentachloride is not surrounded by ten electrons, but three of the chlorine atoms are supposed to be attached to the phosphorus atom by ordinary duplets, whereas the other two are joined to it by singlet linkages, making a total of eight electrons round the central atom ; with this arrangement each chlorine atom would still complete its octet. In the same



way sulphur hexafluoride is considered to have all six fluorine atoms joined to the central atom by single electron bonds; the group surrounding the sulphur atom is only a sextet, but there is no reason to doubt its stability, as sextets probably occur in the stable halides of boron. Sugden has also extended the idea of singlet linkages to other compounds and ions, *e.g.*,  $\text{AlF}_6'''$  and  $\text{Co}(\text{NH}_3)_6'''$ , in which more than four atoms or groups are attached to the central atom by covalent bonds.

**Compounds with Singlet Linkages.** There is little doubt that the hydrogen-molecule ion,  $\text{H}_2^+$ , which exists in vacuum discharge tubes, contains a singlet linkage since it only has one electron to unite two hydrogen nuclei. It will be seen later that there are special reasons for the relative stability of the one-electron linkage in this case (p. 68), and these are operative in a very limited number of instances. In any case the heat of dissociation of  $\text{H}_2^+$ , obtained from a study of its spectrum, is about 60,000 cal., compared with a value of 100,000 cal. for the normal hydrogen molecule, so that the single electron bond is obviously much weaker than an ordinary duplet bond.

It appears that boron hydride,  $\text{B}_2\text{H}_6$ , cannot be formulated without the inclusion of two singlet linkages. It has been considered possible that the two electrons in the first quantum level of a boron atom are brought out to take part in the formation of a valency bond; the assumption of single electron links would then not be necessary, but the amount of energy involved can be shown to be so considerable as to render highly improbable the transfer of electrons from the first to the second quantum level. Sidgwick (1927) has proposed the structure



with two hydrogen atoms attached by singlet linkages, and Pauling (1931) considers that from the standpoint of wave mechanics such a formula is possible, although he regards it as one of a series of "resonance" states in which there is a continual



interchange of the linkages attaching the hydrogen atoms to the boron atoms (p. 69). Lewis (1933), who "doubts if there is a single case known of a stable chemical substance in which there is good evidence for the one-electron bond," has gone a stage further and suggested that  $B_2H_6$  has a structure like ethane except for two missing electrons, and that six electron *pairs* oscillate between seven possible positions. This would result in a molecule with all electrons in pairs, but each bonding pair of "orbits" is only occupied six-sevenths of the time; in this way the strength of the bonds is diminished, although the molecule retains some stability. Such a compound would be diamagnetic, whereas if the Sidgwick formula were correct it should be paramagnetic; investigation by Farkas and Sachsse (1934) has shown that the boron hydride  $B_2H_6$  is actually diamagnetic. A conclusion similar to that of Lewis has been reached by Mulliken (1935), who employed the wave-mechanical treatment known as the method of molecular orbitals (p. 58); the latter author suggests that each boron atom has five bonding electrons available which are shared equally between three hydrogen atoms. A structure of this type would be diamagnetic. It is clear that although the electronic structure must be written, for simplicity, in the way proposed by Sidgwick, actually the single-electron bonds cannot be regarded as true singlet linkages. In any case it must be remembered that boron hydride is very unstable; it gives off hydrogen on warming gently, and is readily decomposed by water. It may be concluded, therefore, that the singlet linkage, if it is present, is associated with marked instability. As already indicated, however, sulphur hexafluoride, in which Sugden supposes the presence of six one-electron bonds, is remarkably stable. Other aspects of the subject of singlet linkages will be considered towards the end of the present chapter (p. 68), and also in Chapter II., wherein it is shown that the arguments based on parachors are not completely convincing.

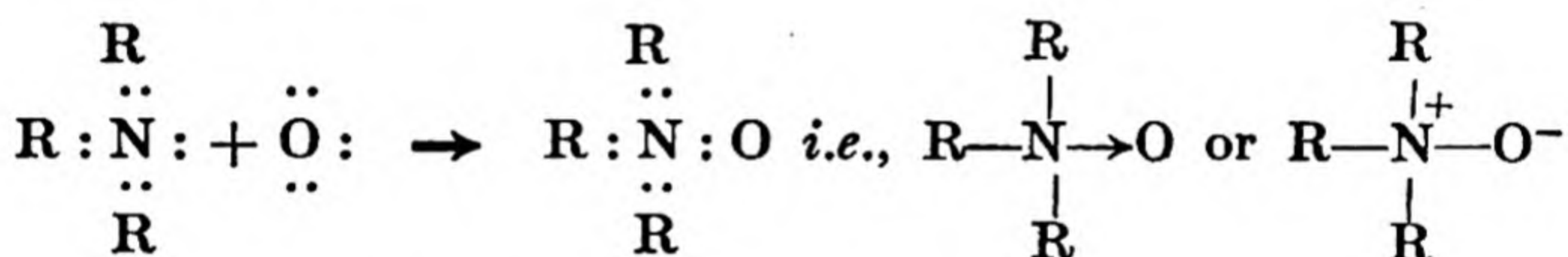
### THE SEMI-POLAR LINKAGE

In the formation of a semi-polar link it is necessary that the donor should have a pair of electrons, *i.e.*, a "lone pair," available



which are not shared with any other atom; the acceptor must either require a pair of electrons in order to complete its octet, or else it must be capable of increasing its valency group of electrons to numbers exceeding eight. In some instances both the donor and acceptor are capable of independent existence, and so this type of semi-polar bond, which may be called a co-ordinate link, is fairly readily broken. In others, however, where separate stability is not possible, the bond is as strong as an ordinary linkage, and apart from the presence of an appreciable electrical dipole it is indistinguishable from a normal covalency; examples of the latter type of semi-polar bond will be considered first.

The oxygen atom has only six electrons, and so it is very ready to accept a pair of electrons from a suitable donor in order to complete its octet; the resulting linkage is one of reasonable stability. Such compounds, *e.g.*, the amine oxides, are formed when tertiary amines, which all possess a lone pair of electrons, act as donors, thus

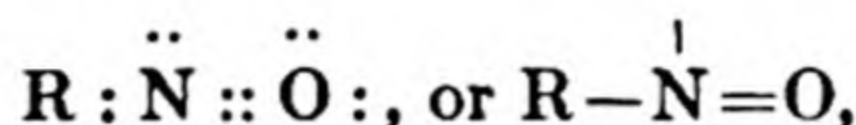


In the old method of formulation such an amine oxide would be represented as  $\text{R}_3\text{N}=\text{O}$ , with a double bond, but reason will be given for considering that a semi-polar linkage behaves, stereochemically at least, as if it were a single bond (p. 36; see also p. 254). It is reasonable to inquire why the  $\text{NH}_3$  molecule is not able to donate a pair of electrons to an oxygen atom, for  $\text{H}_3\text{N}^+-\text{O}^-$  appears to be unknown. The electron-attracting tendency of the hydrogen atoms is evidently sufficient to hold the lone pair entirely to the nitrogen atom; if the hydrogens are replaced by alkyl groups, which have an electron repelling capacity (cf. p. 158), the donating power of the nitrogen will obviously be increased.

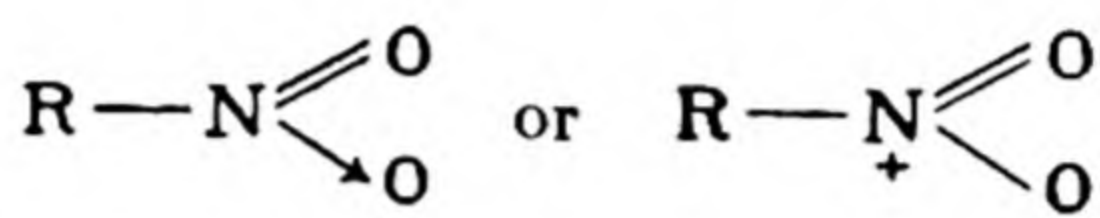
Another instance of the  $\text{N}^+-\text{O}^-$  semi-polar link is found in nitro-compounds; although the nitrogen has completed its



octet in the nitroso compounds it has a lone pair of electrons, thus



which it is able to donate to an oxygen atom and so complete the octet of the latter. There is good reason to believe, therefore, that the formula for a nitro-compound should be written



(see also p. 113). This type of structure suggests a dissymmetry which apparently does not exist (see p. 168); it is probable that two identical structures, except that the nitrogen-oxygen bonds are interchanged, account for the actual symmetry (p. 92).

**Polar Properties.** In the earlier discussion of the semi-polar bond (p. 16) it was shown that this type of linkage leads to the presence of an electrical dipole in the resulting molecules. This implies that such compounds will have a much larger external field than those containing ordinary covalencies, and consequently, in accordance with what has already been said (p. 23), the former should be less volatile than the latter. To obtain evidence in favour of this deduction Sidgwick (1927) compared the boiling points of nitrites ( $\text{R}-\text{O}-\text{N}=\text{O}$ ) and of the isomeric nitro-compounds  $\left( \text{R} - \overset{+}{\text{N}} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{O}^- \end{array} \right)$ ; his figures are given in Table VII.

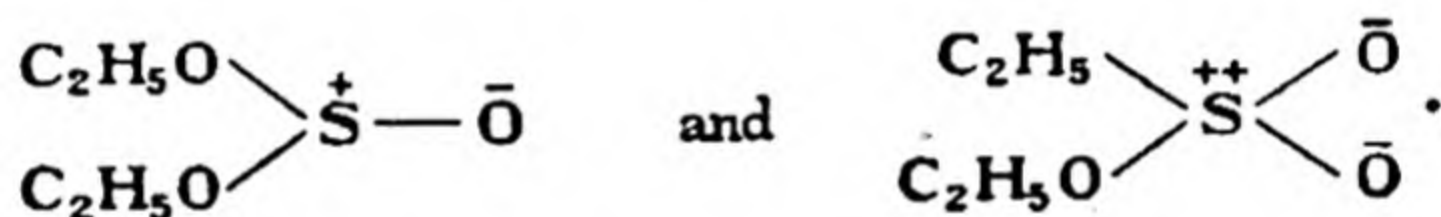
TABLE VII.

*Boiling Points of Isomeric Nitrites and Nitro-compounds  
at 1 Atm. Pressure*

	Nitro.	Nitrite.	Difference.
$\text{CH}_3 \cdot \text{NO}_2$ .      .	101°	-12°	118°
$\text{C}_2\text{H}_5 \cdot \text{NO}_2$ .      .	114°	17°	97°
$\text{C}_4\text{H}_9 \cdot \text{NO}_2$ .      .	152°	75°	77°

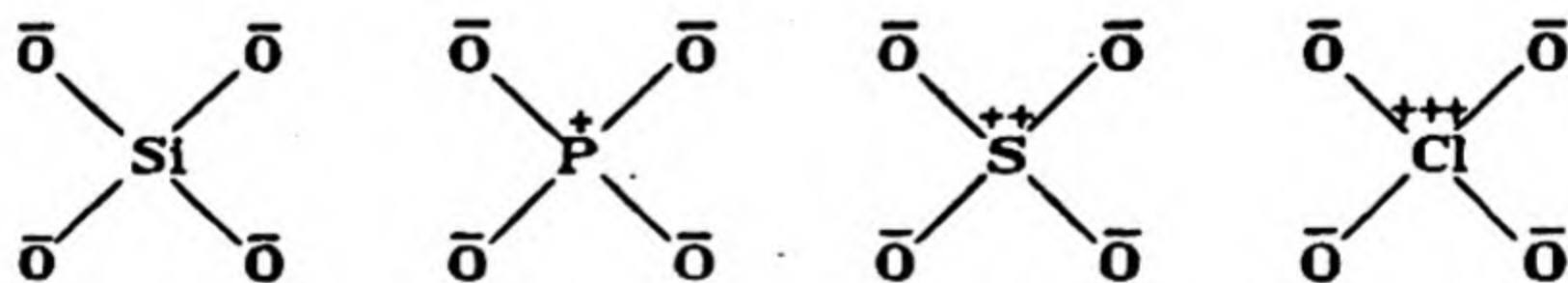
Owing to the presence of a dipole resulting from the semi-polar link, the boiling point of nitrobenzene ( $208^\circ$ ) is higher than that of chlorobenzene ( $132^\circ$ ) and of bromobenzene ( $155^\circ$ ); similarly trimethylamine oxide,  $(\text{CH}_3)_3\overset{+}{\text{N}}-\overset{-}{\text{O}}$ , is a solid which decomposes without melting at  $180^\circ$ , but the isomeric  $\beta$ -methylhydroxylamine ethyl ether,  $(\text{CH}_3)\cdot\text{NH}\cdot\text{O}\cdot\text{C}_2\text{H}_5$ , boils at  $65^\circ$ .

It will be seen in Chapter III. that a compound containing a dipole must have an exceptionally high dielectric constant, and hence this should be another property of compounds containing the semi-polar bond. As examples may be mentioned the values for nitrobenzene and nitromethane, 36 and 39 respectively, compared with constants of 10, and less, for esters, ethers and hydrocarbons. Of the two isomeric compounds with the formula  $(\text{C}_2\text{H}_5)_2\cdot\text{SO}_3$ , one contains a single semi-polar link, whereas the other has two, thus,



The dielectric constants are 16 and 42, respectively, the difference being in accordance with expectation.

**The Oxy-Acids.** The semi-polar link is frequently encountered in the oxides and oxy-acids of various elements; the series of ions of the type  $\text{XO}_4$  formed by silicon, phosphorus, sulphur and chlorine, thus



is particularly interesting (Lowry, 1923). It will be observed that the *net* valency of the anions decreases regularly in the series from four to one, as the number of valency electrons of the central atom increases from four to seven. In each of these ions the oxygen atoms may be regarded as being associated with nine electrons (cf. p. 16)—two in the first and seven in the second quantum group—and as the nuclear charge is eight, they may all be



considered to be negatively charged. The number of electrons associated with each of the central atoms is fourteen—two in the first quantum group, eight in the second and four in the third—and since the nuclear charges are fourteen for silicon, fifteen for phosphorus, sixteen for sulphur and seventeen for chlorine, it follows that the silicon atom is uncharged, whereas the others carry one, two and three positive charges respectively. The ions thus acquire the configurations represented above, having net charges in agreement with experimental observations. This method of representation brings out the essential symmetry of the ions, since all the oxygen atoms in any particular ion may be regarded as equivalent.

**Stereochemistry of the Semi-polar Linkage.** Using the older valency principles a semi-polar link would be represented by a double bond, and although it may be counted *numerically* as two linkages when computing the classical valency, it behaves physically as if it were a single bond. This has been definitely established mainly as the result of stereochemical studies with sulphur compounds (Phillips, 1925 ; Bennett, 1927 ; Mann, 1930).

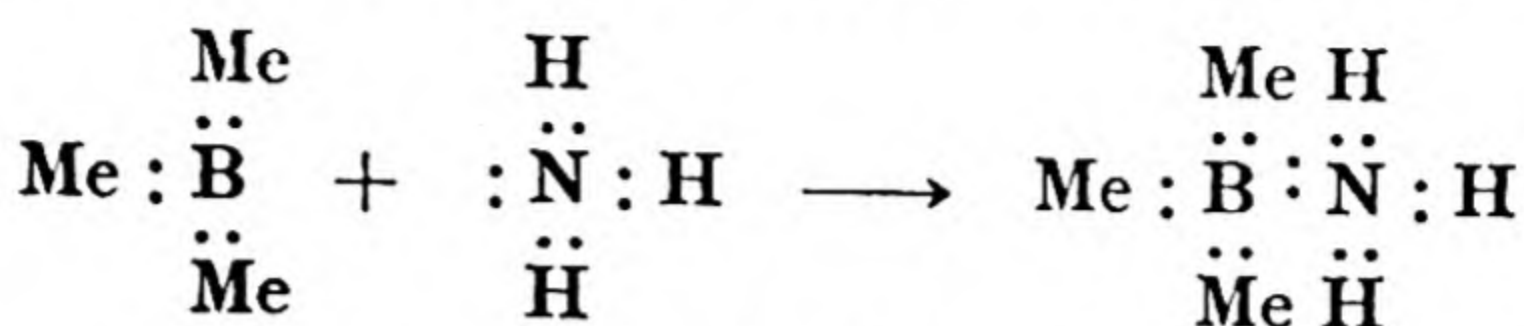
## THE CO-ORDINATE LINK

As already explained (p. 17), the term “co-ordinate” is being used here for the type of semi-polar bond represented by an arrow indicating the actual process of the transfer of a pair of electrons from one atom to another. Generally, although not always, this type of linkage unites two molecules both of which are capable of a separate existence ; it occurs, as the name implies, particularly in the co-ordination compounds studied by Werner. Before discussing these, however, brief mention will be made of certain molecular compounds the existence of which can be readily accounted for by the electronic theory of valency.

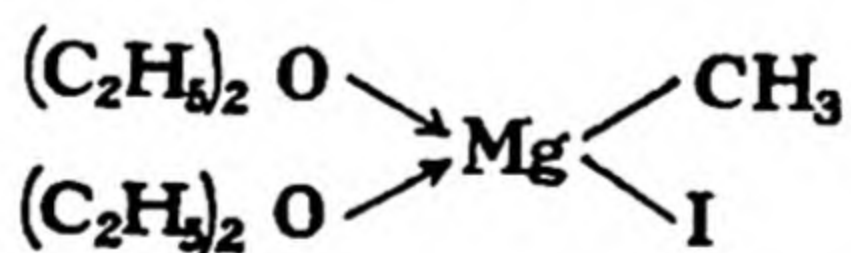
**Molecular Compounds.** Although the electron octet is regarded as the criterion of stability some molecules, particularly those of compounds of boron, possess only a sextet of electrons ; such a molecule is able to act as an acceptor of a pair of electrons forming a molecular compound with a co-ordinate link. The boron shell



in boron trimethide has only six electrons, and so it is able to accept the lone pair of electrons from ammonia, thus



that is,  $\text{Me}_3\text{B} \leftarrow \text{NH}_3$  or  $\text{Me}_3\text{B}^--\text{NH}_3^+$ ; this is a fairly stable compound, both nitrogen and boron atoms having complete octets. In the same way boron trichloride or trifluoride form the following compounds:  $\text{Cl}_3\text{B} \leftarrow \text{AsH}_3$ ,  $\text{Cl}_3\text{B} \leftarrow \text{PCl}_3$  and  $\text{F}_3\text{B} \leftarrow \text{OEt}_2$ , and others; in each case the boron atom accepts an unshared pair of electrons from an atom with a complete octet. In the simple form of aluminium chloride,  $\text{AlCl}_3$ , the aluminium atom has only a sextet of electrons, and consequently it forms a co-ordination complex with antimony trichloride, since the antimony atom, like nitrogen, phosphorus and arsenic in similar compounds, has a lone pair of electrons; this compound is probably of exactly the same type as the boron compounds already discussed, viz.,  $\text{Cl}_3\text{Al} \leftarrow \text{SbCl}_3$ . The compound between magnesium methyl iodide and ether, in the Grignard reagent, is probably formed as the result of the donation of a lone pair of electrons from each of the oxygen atoms in two molecules of ether to the magnesium atom, thus



In this manner the octet of the magnesium atom is completed.

It is well known that many organic substances form "molecular compounds": for example, nitro-derivatives form compounds with hydrocarbons and with amines; carbon tetrachloride unites with acetone, ethyl acetate and ether; chloroform combines with methyl alcohol, ether, acetone and many bases. According to Lowry (1924) and Bennett (1929) it is very probable that in all these compounds one of the components acts as donor and the other as acceptor, so that a co-ordinate link is formed. In ethers, ketones and esters the oxygen atom has two lone pairs of electrons and,

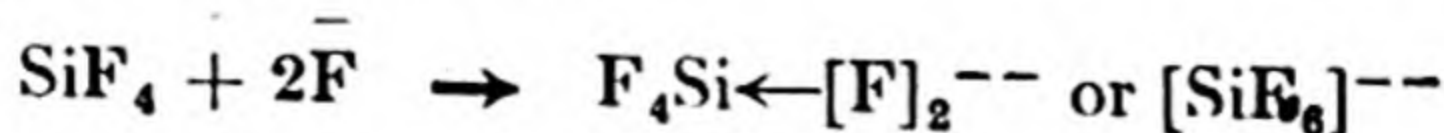


under the influence of the electron-repelling groups in the same molecule, these may be donated to an appropriate acceptor. In chloroform, bromoform and iodoform the hydrogen atom apparently acts as acceptor of electrons, forming co-ordinated hydrogen which is considered later (p. 47). With carbon tetrachloride the chlorine appears to accept the pair of electrons from an oxygen atom: this would mean that the halogen can increase its outer group of electrons beyond the usual octet (Earp and Glasstone, 1935). This tendency, as might be anticipated, increases with increasing size of the halogen atom.

**Double Halides.** The formation of a complex halide may be considered as a type of co-ordination, since a stable molecule and a stable ion are involved; thus the borofluoride ion is produced when a fluorine ion, with a unit negative charge and an electron octet, donates a pair of electrons to the boron atom and permits the latter to complete its octet, thus



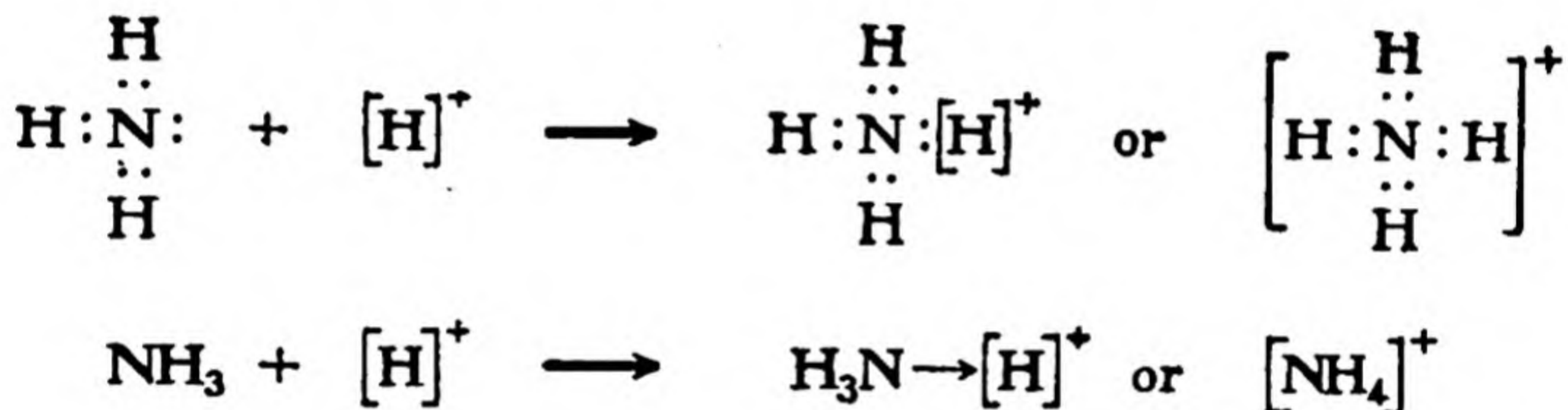
It must not be imagined that in the borofluoride ion there is any difference between one fluorine atom and the other three; the co-ordinate link cannot be distinguished from the others, and the formula must be written  $\text{BF}_4^-$ ; the negative charge, as may be seen by counting the number of electrons associated with each atom and comparing with its nuclear charge, actually resides in the boron atom, the fluorine atoms being uncharged. A similar type of ion is formed from silicon tetrafluoride, although in this case the original substance has its valency octet complete; in the resulting silico fluorides it appears that the valency group of the silicon atom is increased to twelve by the donation of two electron pairs from two fluorine ions:





The stability of the  $\text{SiF}_6^{--}$  complex is considerable, and the problem of its structure is analogous to that of sulphur hexafluoride, to which reference has already been made. It is perhaps significant that the  $\text{TiF}_6^{--}$  ion is even more stable than  $\text{SiF}_6^{--}$ ; since the titanium atom is larger than the silicon atom the former would accommodate the group of twelve electrons more readily. The formation of the  $[\text{AlF}_6]^{--}$  ion from  $\text{AlF}_3$  and  $3\text{F}^-$  is similar to that of the complex fluorides already discussed.

**The Ammonium Ion.** An analogous mechanism may be regarded as applying to the production of the ammonium ion; here the lone pair from the nitrogen atom in ammonia is donated to a hydrogen ion (proton), which has no electrons, thus

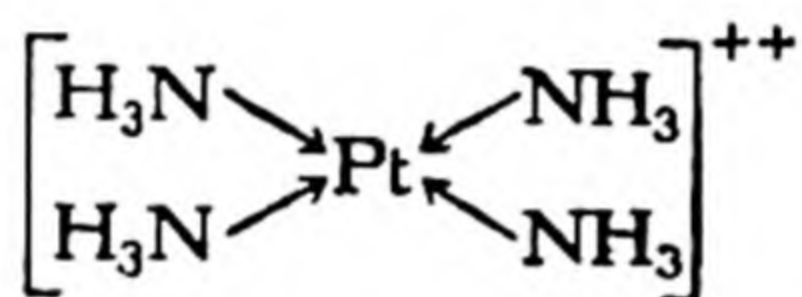


There is, of course, no difference between the hydrogen to which the electron pair has been donated and the others, and so the formula is rarely written  $\text{H}_3\text{N} \rightarrow [\text{H}]^+$ ; this may, however, represent an intermediate stage in the formation of an ammonium ion by the union of an ammonia molecule and a proton, *e.g.*, in the neutralisation of a solution of ammonia. In the stable ammonium ion the positive charge—as in all cases of four-covalent nitrogen—is actually on the nitrogen atom.

**The Platinous Ammines.** The electronic theory has provided a very helpful interpretation of Werner's theory of valency as applied to complex compounds of metals; the principal valency of Werner is now identified with the electrovalency of the element, *i.e.*, with the number of electrons which the atom transfers completely to anions, whereas the co-ordination number represents the covalency. The co-ordination number six, which occurs frequently, implies that the central atom can form six covalencies, and thus can accommodate a group of twelve electrons; if the idea of



singlet linkages is accepted, however, the co-ordination number of six would imply only an electron sextet. The co-ordination number of four is supposed to require an electron octet, irrespective of whether the linkages are duplets or singlets. The case of the ammines of platinum will be considered as an example to illustrate the application of the electronic theory. In the compound  $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$  the co-ordination number of platinum is four, and its principal valency two; since conductance measurements indicate that the compound dissociates into three ions it may be regarded, as Werner proposed, as  $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$ ; the positive ion complex is enclosed in square brackets. This ion may be regarded as being formed as a result of four ammonia molecules, each of which possesses a lone pair of electrons, donating that pair to the platinous ion ( $\text{Pt}^{++}$ ), thus



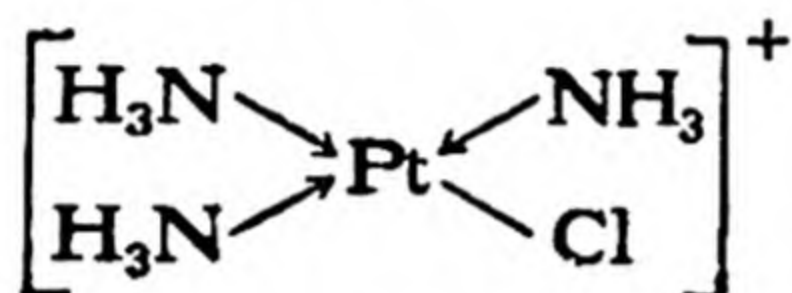
No electrons are transferred to or removed from this complex, so that the charge on the resulting ion, two positive, remains unchanged; the complex platinammine ion can thus unite in an electrovalent manner with two chlorine ions to form the salt under discussion.

It will be noted that the platinum atom had originally 78 outer electrons; two of these are lost in the formation of the platinous ion, whereas eight are gained from the ammonia molecules making a total of 84 electrons. The radioactive "emanation" possesses 86 electrons, and so the platinum atom approaches a stable electronic structure. Theoretically, the complete set of 86 electrons could be acquired if the platinum had a co-ordination number of five, with an electrovalency of two; for reasons which are not clear such compounds do not exist. The co-ordination number of five is in fact somewhat exceptional, except perhaps with the halides of Group V.

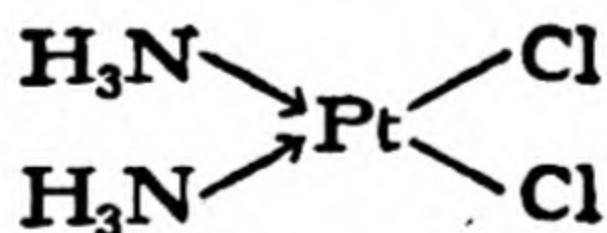
By suitable means one of the ammonia molecules in the tetrammine may be eliminated leaving  $\text{Pt}(\text{NH}_3)_3\text{Cl}_2$ , but this



compound ionises to give two ions, and one of the chlorine atoms cannot be precipitated by silver nitrate. The structure is evidently  $[\text{Pt}(\text{NH}_3)_3\text{Cl}]\text{Cl}$ , the co-ordination number of four being maintained. The three ammonia groups are still attached by a co-ordinate link, as before, but the chlorine atom with its seven outer electrons is only able to contribute one towards an electron pair, the other being supplied by the platinum atom ; the number of electrons surrounding the latter thus becomes 78 plus 6 (for the  $3\text{NH}_3$  groups), and plus 1 (for the chlorine atom), that is 85. This is one more than the group of 84 which is apparently stable for the platinum ion, and so the complex tends to lose one electron to form a univalent positive ion :



On the elimination of another  $\text{NH}_3$  group the resulting compound  $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$  is found to be a non-electrolyte, and hence both chlorine atoms must be attached to the platinum atom by covalent linkages. The total electron groups of the platinum are then as follows : platinum atom 78, plus 4 donated by  $2\text{NH}_3$  groups, plus 2 from two chlorine atoms, that is 84 electrons altogether. This yields the stable electronic arrangement, and there is no further tendency to lose or gain electrons ; the compound is entirely covalent and may be represented as



The next stage in the platinous ammine series is the compound  $\text{Pt}(\text{NH}_3)\text{Cl}_3\text{K}$  ; this dissociates into two ions, the potassium being positive and the  $[\text{Pt}(\text{NH}_3)\text{Cl}_3]$  complex the univalent negative ion. In the formation of the latter the number of electrons involved is  $78 + 2 + 3 = 83$ , which is one fewer than the stable number 84 ; the group will, therefore, tend to gain an electron and so form a univalent anion able to unite in an electrovalent fashion with a potassium ion. In the next compound  $\text{K}_2[\text{PtCl}_4]$  the removal of



the last  $\text{NH}_3$  radical leaves the  $[\text{PtCl}_4]$  group with 82 electrons, and it acquires stability by gaining two more to form the  $[\text{PtCl}_4]^{--}$  ion.

**The Platinic Ammines.** In the platinic state (quadri-electrovalent) platinum has a co-ordination number of six, and is presumably able to form a group of twelve electrons; the platinichlorides, *e.g.*,  $\text{K}_2[\text{PtCl}_6]$ , are compounds in which these values are applicable. In the group  $[\text{PtCl}_6]^{--}$ , which is presumably stable, the number of electrons is as follows: 78 for the platinum atom, 6 contributed by the six chlorine atoms towards six shared duplets, and 2 further electrons giving the double negative charge, making a total of 86 electrons. This is the same number as in the inert gas "emanation," and is apparently only possible when the platinum has an outer group of twelve electrons, or six electrons if the linkages are singlets, but not with a group of ten, as would be required for bi-electrovalent (platinous) platinum. As the chlorine atoms in the platinichloride are replaced by  $\text{NH}_3$  groups, the number of electrons associated with the complex increases, and in  $\text{PtCl}_4(\text{NH}_3)_2$  there are already 86 electrons around the central atom, and no further tendency to gain or lose electrons should exist. This compound, as might be anticipated, is completely covalent and hence a non-electrolyte. In the extreme radical of the series, *viz.*,  $\text{Pt}(\text{NH}_3)_6$ , there are 90 electrons, and so this arrangement will tend to lose four electrons and form a cation with four positive charges,  $[\text{Pt}(\text{NH}_3)_6]^{++++}$ , capable of uniting by electrovalencies with anions containing an equivalent charge; the compounds  $[\text{Pt}(\text{NH}_3)_6](\text{CO}_3)_2$  and  $[\text{Pt}(\text{NH}_3)_6](\text{OH})_4$  comply with this requirement.

From the treatment developed it may be seen that the number of electrons required for stability in any metal complex may be determined by adding to the normal number of outer electrons twice the co-ordination number, since every neutral co-ordinated group donates two electrons, and subtracting the ordinary electrovalency of the central atom. The result has been called by Sidgwick the "effective atomic number," which is abbreviated to E.A.N. The values given in Table VIII. have been calculated for a number of elements; the co-ordination numbers and principal



valencies quoted all correspond to known complex compounds. The number of electrons in the nearest inert gas is given for purposes of comparison in each case.

TABLE VIII.—*Number of Electrons in Stable Complexes.*

Element.	No. of Electrons.	Co-ordination Number.	Valency.	E.A.N.	Inert Gas.
Chromium .	24	6	3	33	36
Iron (ferric) .	26	6	3	35	
Iron (ferrous) .	26	6	2	36	
Cobalt . .	27	6	3	36	
Nickel . .	28	6	2	38	
Nickel . .	28	4	2	34	
Copper . .	29	4	2	35	
Zinc . .	30	4	2	36	
Zinc . .	30	6	2	40	54
Molybdenum .	42	8	4	54	
Rhodium .	45	6	3	54	
Palladium .	46	4	2	52	
Iridium .	77	6	3	86	86
Platinum (ic) .	78	6	4	86	
Platinum (ous)	78	4	2	84	
Gold . .	79	4	1	86	

On the whole the stable electron groupings of complex ions approach those for the inert gases; the discrepancy of two electrons in platinous platinum is also found with palladium, with quadri-covalent nickel and with chromium. The numbers 38 for nickel and 40 for zinc in the hexa-covalent form seem, however, difficult to understand, as a stable arrangement with electrons in excess of the inert gas number might not be expected. It must be remembered, however, that the actual electronic arrangement, even in the platinic compounds, probably is not the same as in the inert gas. A co-ordination number of six implies a group of twelve (or six, if singlets) equivalent electrons in the outermost layer, whereas the inert gases apparently have eight such electrons.

**Metallic Carbonyl Compounds.** The metallic carbonyls are probably to be regarded as co-ordination compounds in which the carbon monoxide behaves as a neutral radical, the carbon



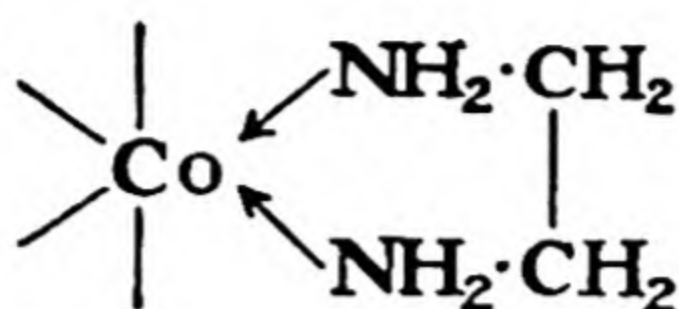
atom donating a pair of electrons to the metal, thus  $M \leftarrow CO$ . As the result of the examination of a number of such compounds, Sidgwick and Bailey (1934) have noticed an interesting regularity: the difference between the E.A.N. of the metal atom and the atomic number of the next inert gas is always one less than the number of metallic atoms in the molecule. For a carbonyl having the general formula  $M_x(CO)_y$ , this result can be expressed as the relationship

$$g - (mx + 2y)/x = x - 1,$$

where  $m$  and  $g$  are the atomic numbers of the metal and the inert gas, respectively; the quantity in the bracket is, of course, the effective atomic number. When  $x$  is unity, the E.A.N. is exactly equal to the number of electrons in the inert gas, as was first shown to be the case by Langmuir (1921) for the carbonyls of chromium, iron, nickel, molybdenum and tungsten. For carbonyls containing more than one metallic atom in the molecule, *e.g.*,  $Fe_2(CO)_9$ ,  $Fe_3(CO)_{12}$ ,  $Co_2(CO)_8$  and  $Co_4(CO)_{12}$ , the E.A.N. is apparently less than the inert gas number: this probably means that actually the E.A.N. is equal to the expected value, and the apparent discrepancy is due to the fact that some of the CO groups supply more than two electrons. This condition would be satisfied if in certain cases donation occurred through the oxygen as well as the carbon, thus  $M \leftarrow CO \rightarrow M$ , the CO molecule acting as a bridge between two metal atoms.

**Other Co-ordination Compounds—Chelate Groups.** The  $H_2O$  group can act as a neutral radical, since the oxygen atom can donate one of its two lone pairs, in the so-called aquo-compounds, *e.g.*,  $[Co(NH_3)_5(H_2O)]Cl_3$ . Iso-nitrile groups, *e.g.*,  $CH_3NC$ , frequently occur in complex compounds and presumably the lone pair of electrons on the carbon atom of the  $-NC$  group is able to form a co-ordinate link. Various amines, *e.g.*, pyridine, methylamine, etc., can replace the  $NH_3$  group in ammines, and an ethylene diamine molecule,  $NH_2 \cdot CH_2 \cdot CH_2 \cdot NH_2$ , is able to replace two  $NH_3$  groups, since each nitrogen atom can contribute a lone pair, and so “chelate,” or claw-like, compounds (Morgan, 1920) of the type



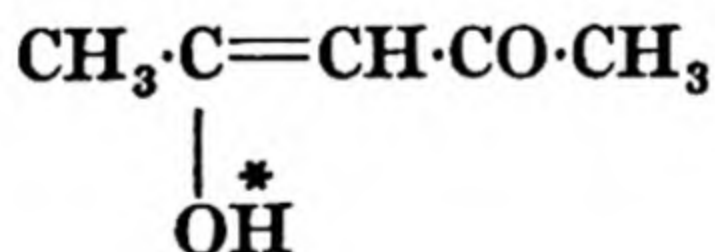


are obtained. The principle involved is, however, identical with that concerned in the simple ammines and aquo-compounds.

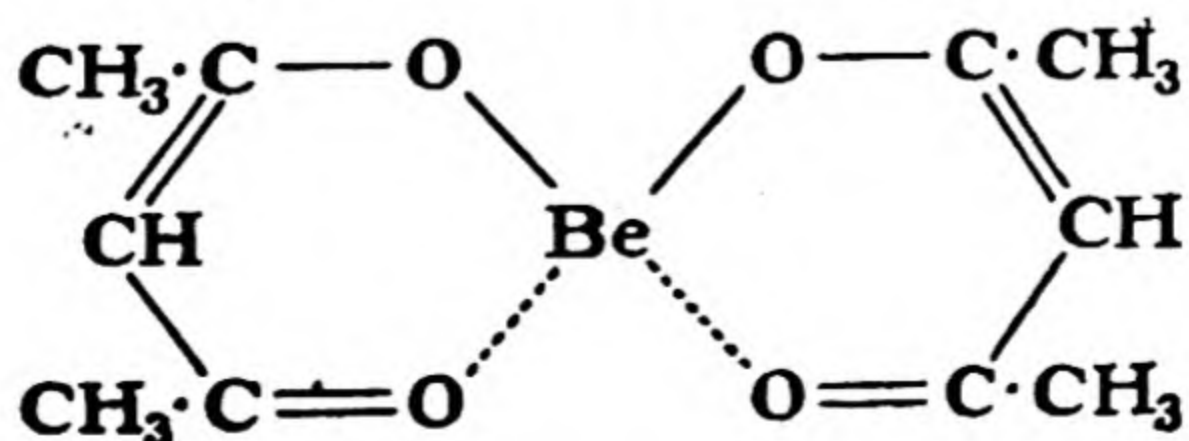
The electronic theory is thus able to account in a very satisfactory manner for Werner's formulation of complex compounds, and for his statement that the introduction of a neutral group, that is one with complete octets, *e.g.*,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$  or even  $\text{CH}_3\cdot\text{NC}$ , does not affect the valency of the central atom, but the insertion of each univalent negative radical reduces the effective positive charge by one unit.

### COVALENT COMPOUNDS OF METALS

There is an important group of metallic derivatives of organic compounds, mainly  $\beta$ -diketones and  $\beta$ -keto-acids, to which Werner applied his theory although it did not appear convincing until the development of the electronic views on valency. Many metals form derivatives of acetylacetone, presumably by replacing a hydrogen atom (marked \*) in the enolic form of the latter compound :



For example, beryllium forms  $\text{Be}(\text{C}_5\text{H}_7\text{O}_2)_2$  and aluminium gives  $\text{Al}(\text{C}_5\text{H}_7\text{O}_2)_3$ ; these compounds have low melting points, volatilise without decomposition, are sparingly soluble in water and dissolve readily in hydrocarbons. They are obviously not salts, and Werner suggested they were compounds of the type

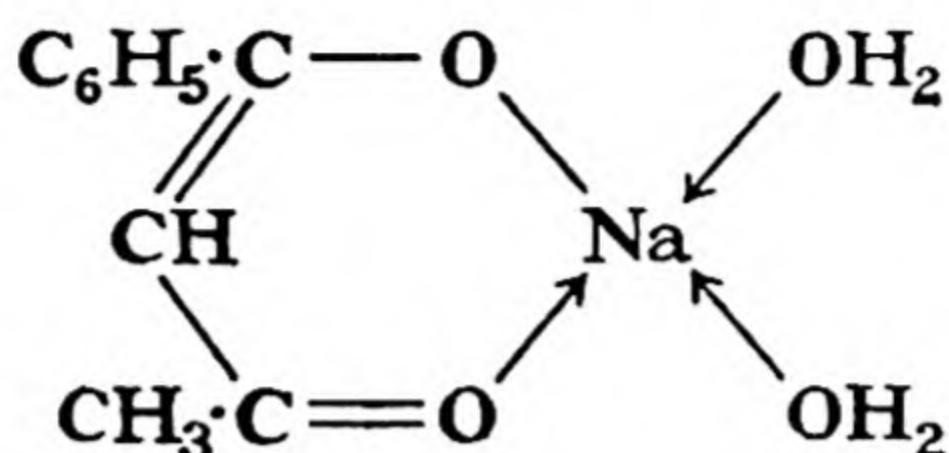








original substance is insoluble in toluene the di-hydrate is quite soluble and so probably has a covalent structure, thus



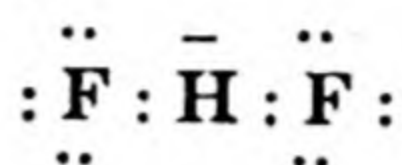
The sodium atom contributes its own electron towards one shared duplet, and its octet is completed by the donation of one electron pair from the oxygen atom of the  $-\text{C}=\text{O}$  group, and two pairs from the oxygen atoms of the water molecules. The sodium atom can thus be uni-electrovalent or quadri-covalent. Similar compounds of the sodium salt of chelated *o*-hydroxybenzaldehyde with two molecules of water or ether have been claimed by Brady and Bodger (1932). The formulation of such compounds, and in fact their general structure, would have been a very difficult problem before the development of the electronic theory of valency.

### CO-ORDINATED HYDROGEN

**Hydrogen Fluoride.** The subject of co-ordinated hydrogen is so remarkable that it is worthy of special treatment. Evidence has accumulated in recent years (Moore and Winmill, 1912 ; Latimer and Rodebush, 1920 ; Lowry, 1923 ; Sidgwick, 1924) which points to the fact that a hydrogen atom, already joined in a stable manner by a pair of electrons to another atom, is capable, under certain conditions, of accepting another pair of electrons. This occurs more particularly if the hydrogen atom is attached in the first place to a strongly electronegative element, *e.g.*, oxygen, nitrogen or fluorine. Hydrogen fluoride is associated in the vapour state and exists mainly as  $\text{H}_2\text{F}_2$  molecules, and even in solution it gives rise to salts like  $\text{KHF}_2$ , ionising to form  $[\text{HF}_2]^-$  ions. This ion apparently results from the union of a hydrogen fluoride (HF) molecule with a fluorine ion; the latter sharing one of its lone pairs either with the hydrogen or the fluorine atom of the  $\text{H}-\text{F}$  molecule. There is no evidence whatever from other compounds to

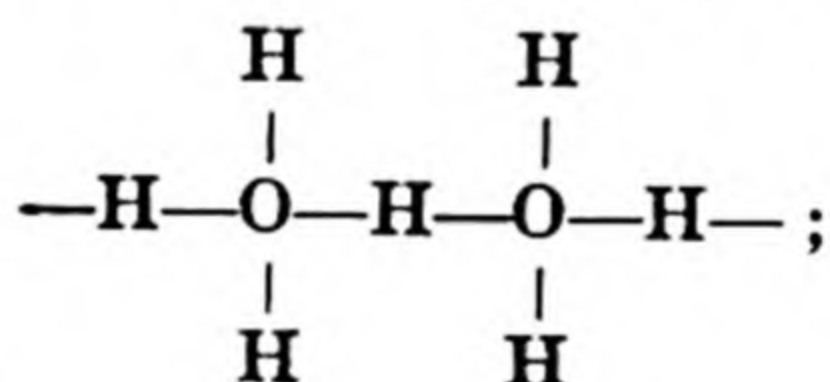


show that fluorine can increase its electron group above eight, and so it appears that the hydrogen atom in some way takes up a pair of electrons from the fluorine ion; the complex  $\text{HF}_2^-$  ion may then be represented by

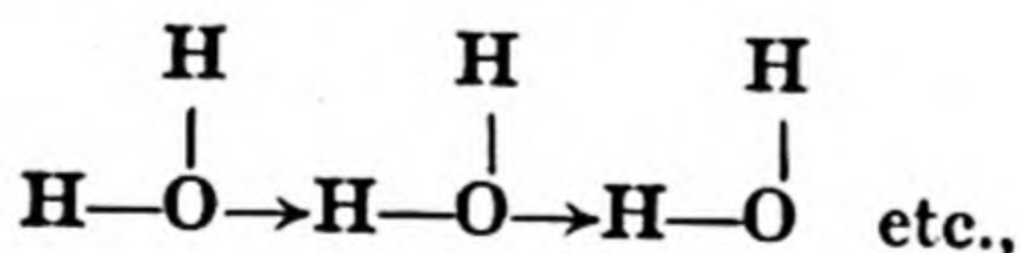


It may appear strange that similar ions are not formed with the other halogen hydrides, but it is known that elements always tend to show their highest possible covalency when combined with fluorine; thus  $\text{SF}_6$  and  $\text{OsF}_8$  are known, but analogous compounds do not occur with the other halogens.

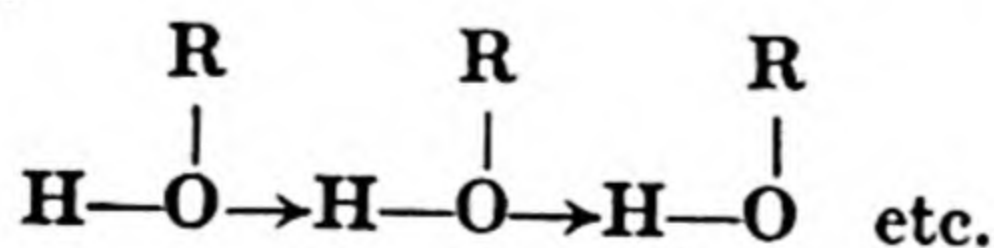
**Association of Hydroxylic Compounds.** Lowry has pointed out the implication of the fact that X-ray analysis of ice shows each atom of hydrogen to be symmetrically placed between two oxygen atoms, whereas each oxygen atom is surrounded by four hydrogen atoms. This structure may be represented as



it indicates that the hydrogen can be an apparently bivalent element. Sidgwick has used this concept to account for the association that is almost invariably observed with compounds containing the  $-\text{OH}$  group; it is supposed that the oxygen atom can donate a pair of electrons to the hydrogen atom belonging to another molecule, thus for water



and for an alcohol,



In these compounds, as well as in hydrogen fluoride, the donor and acceptor are present in the same molecule; but this is not neces-



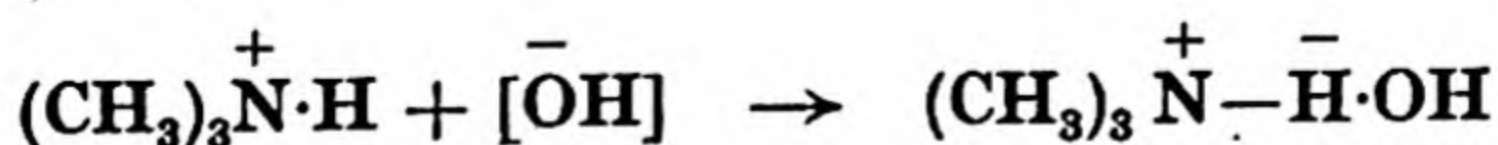
sarily so always ; thus, there is reason to believe that an oxygen atom in an ether can combine with hydroxylic derivatives to form compounds of the type  $R_2O \rightarrow H \cdot O \cdot R'$ . Such compounds probably account for the solubility of ethers in water, and provided other conditions are equal the solubility will increase the more the tendency of the R groups in the ether to repel electrons ; this repulsion will enhance the donating power of the oxygen atom. Bennett and Phillip (1928) have studied the solubility of ethers in water, and have confirmed the view that the presence of electron-repelling groups tends to increase the solubility ; the evidence is thus in favour of the existence of co-ordinated hydrogen. This type of linkage is also probably to be found in the well known phenol-amine compounds, which may be represented as  $Ar \cdot O \cdot H \leftarrow NH_2 \cdot R$ , the nitrogen acting as donor, and in the compounds between chloroform and ethers or ketones, in which the oxygen is the donor.

**Dissociation Constants of Bases.** Moore and Winmill (1912) studied the dissociation constants of various ammonium bases and noted a marked difference between the quaternary bases and the others ; some of their results are given in Table IX.

TABLE IX.—*Dissociation Constants of Ammonium Bases.*

	$RNH_2 \cdot OH$	$R_2NH \cdot OH$	$R_3NH \cdot OH$	$R_4N \cdot OH$
$R = CH_3$ .	$4.87 \times 10^{-4}$	$14.21 \times 10^{-4}$	$0.72 \times 10^{-4}$	Strong base ( $>1$ )
$R = C_2H_5$ .	6.73	10.59	7.87	Strong base ( $>1$ )

These authors suggested the view, later developed by Latimer and Rodebush (1920), that as long as there was a hydrogen atom attached to the nitrogen of the base the hydroxyl group could form a covalent bond, thus



and the tendency to ionise would be comparatively small. In the quaternary bases there is no hydrogen atom for the covalent



attachment of a hydroxyl group, and so the latter is compelled to ionise, and the base is a strong one. The possibility of co-ordination of a negative group to a hydrogen atom attached to nitrogen has also been used (Wynne-Jones, 1931) to account for Walden's observations that the halides of primary, secondary and tertiary bases are comparatively weak electrolytes in acetone and other solvents.

**Co-ordinated Hydrogen and Physical Properties.** Important evidence for the view that hydrogen can act as a bridge between two atoms has been obtained by Sidgwick (1924) from an examination of the solubilities in water and the boiling points of a series of *o*-, *m*- and *p*-substituted phenols; it was found that with compounds containing certain active groups, particularly — NO<sub>2</sub>, — CHO and — Cl, the *o*-derivatives were (a) more volatile, (b) less soluble in water and (c) more soluble in benzene than would have been expected. Some of the results upon which these conclusions are based are given in Table X.; the values for *o*- and *p*-cresols, which behave normally, are inserted for purposes of comparison.

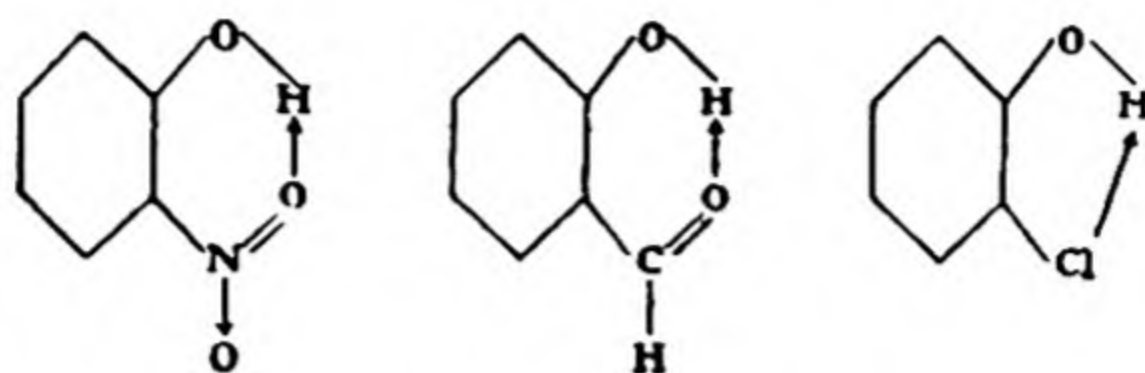
TABLE X.—*Boiling Points and Critical Solution Temperatures of Substituted Phenols.*

Substance.	NO <sub>2</sub> .C <sub>6</sub> H <sub>4</sub> .OH.		Cl.C <sub>6</sub> H <sub>4</sub> .OH.		CH <sub>3</sub> .C <sub>6</sub> H <sub>4</sub> .OH.	
	Ortho.	Para.	Ortho.	Para.	Ortho.	Para.
Boiling Point .	214°	205°	173°	217°	190°	201°
Critical Solution Temperature .	>200°	25°	173°	129°	163°	144°

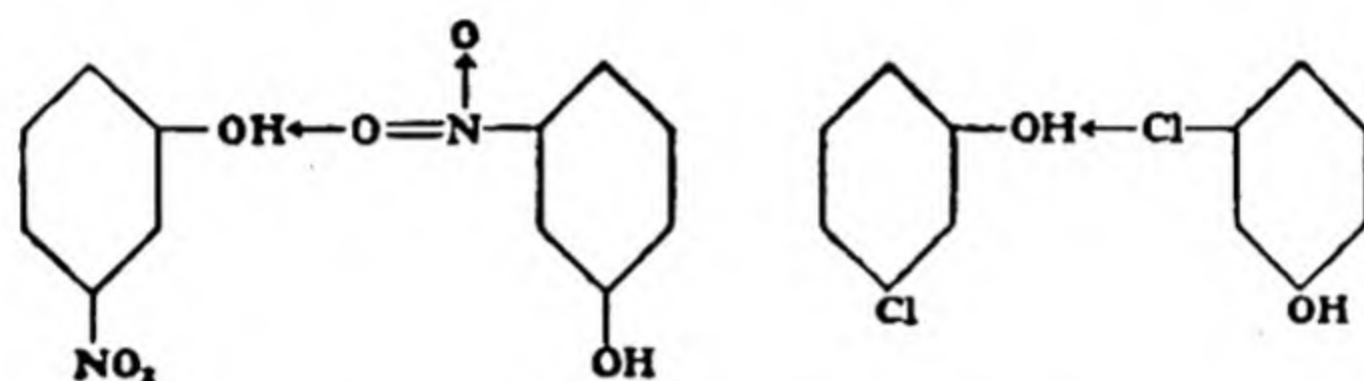
The *o*-nitro- and *o*-chloro-compounds are seen to be more volatile and less soluble in water than would be expected from an examination of the cresols. In other words the *o*- compounds behave exactly as if the hydroxyl group had been suppressed, and this is readily accounted for by the assumption that the oxygen atom of the — NO<sub>2</sub> or — CHO group, or the chlorine atom, donates



a pair of electrons to the hydrogen atom of the — OH group to form a closed ring system, thus



In the *m*- and *p*- compounds, however, the oxygen atom of the — NO<sub>2</sub> or — CHO group in one molecule donates to the hydrogen atom of another, producing associated complexes of the type

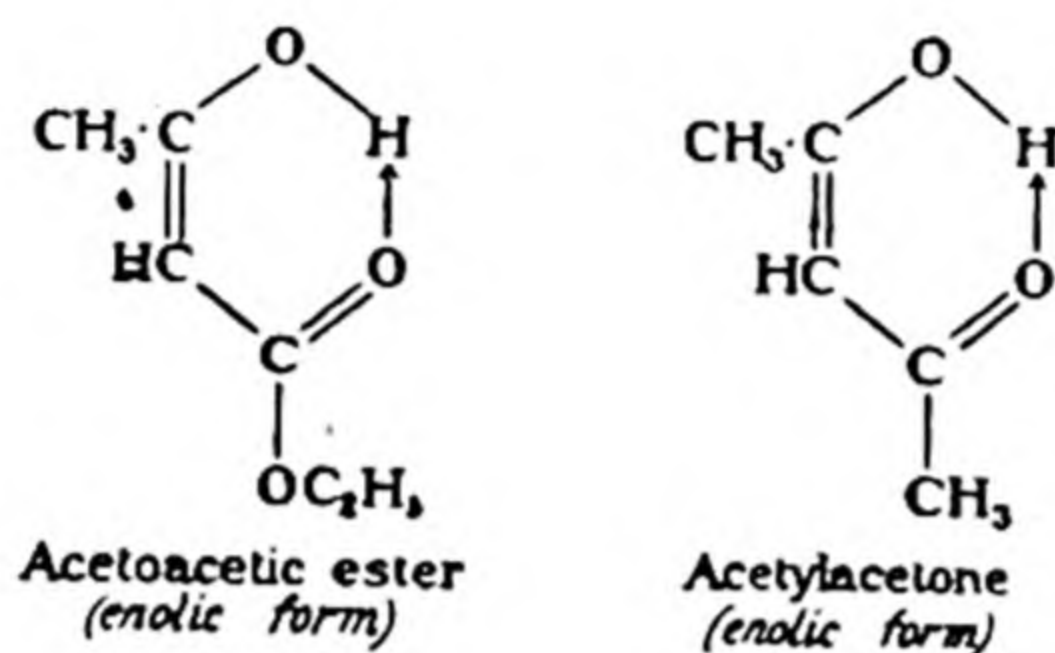


and even more complicated ones, since these double molecules still have a free — OH group. It is clear that in the *o*- compounds, where *intra*-molecular association occurs, the volatility of the more compact molecule will be greater than in the *m*- and *p*- compounds where there is *inter*-molecular association. Similarly the former molecules have their — OH groups suppressed and consequently are sparingly soluble in water, but soluble in non-hydroxylic solvents. If the hydrogen atom of the — OH group is replaced by a methyl group the co-ordination in the resulting ether is not possible, and the properties of the *o*- ethers are very similar to those of the *p*- compounds; these substances are all non-associated, and so have low boiling points and are sparingly soluble in water.

Sidgwick (1925) has also shown that for a number of  $\beta$ -keto-esters, including ethyl acetoacetate, the solubility of the enolic form in hydroxylic solvents is relatively less than in benzene or hexane. This implies that the enolic form cannot contain a hydroxyl group, since hydroxylic compounds are relatively soluble in water and in alcohol, but only slightly soluble in hydrocarbons. Further, Bawn (1932) found that the infra-red spectra



of ethyl acetoacetate and similar esters do not show the characteristic bands which are always associated with the presence of an ordinary — OH group. It seems, therefore, that in agreement with a suggestion made in a somewhat analogous connection by Lowry and Burgess (1923), the hydrogen becomes co-ordinated by accepting an electron pair from an oxygen atom, thus



A review of the evidence leaves little room for doubting that a hydrogen atom can form a co-ordinate link or hydrogen bond, as it is often called... If the hydrogen really accepts a pair of electrons from an atom with which it forms the co-ordinate link then it has a group of four electrons, and this is contrary to the postulate of the Pauli principle. Sugden was of the opinion that each of the two hydrogen valencies is a singlet, so that the group of two electrons for hydrogen is not exceeded; the attachment appears, however, to be too strong to be accounted for by a single electron bond. Another point of view has been developed in recent years, however, which covers the facts in an ingenious manner: this will be considered in connection with the phenomenon of resonance (p. 93).

### COVALENCY MAXIMA

**Sidgwick's Generalisation.** In reviewing the maximum covalency possible for any atom Sidgwick concludes that the values are as follows: for hydrogen **2**; for the elements of the first short period, *i.e.*, lithium to fluorine, **4**; for those of the second short period and the first long period, *i.e.*, sodium to bromine, **6**; and for all elements beyond rubidium **8**. There is some indication that a covalency of ten may be possible with zirconium, cerium and



hafnium in the decahydrates of their acetyl acetone derivatives, but the evidence is by no means decisive. A comparison of these figures with the electronic structure of the elements suggests the following rule (Sidgwick, 1927): a covalency of  $2n + 2$  only becomes possible when there are enough unshared electrons in the atom to fill completely the first  $n$  quantum groups. According to this view a maximum covalency of eight should commence at copper, but actually it does not occur until at least eight places later in the periodic table. There is evidently some reluctance, as is not surprising, to form eight-covalent compounds, since these presumably involve a group of sixteen electrons; such a large group can only occur with the largest atoms. It is a curious fact, for which there is no adequate explanation, that odd covalencies are avoided, especially by heavy-metal atoms (Menzies, 1934). Hydrogen is, of course, generally univalent and nitrogen and boron are frequently ter-covalent; both of the latter elements, however, tend to increase their co-ordination groups to four, thus  $[\text{NH}_4]^+$  and  $[\text{BF}_4]^-$ . A covalency of five is known with certainty in the halides of Group V., *e.g.*,  $\text{PCl}_5$ ,  $\text{SbCl}_5$ , but rarely elsewhere, *e.g.*,  $\text{IF}_5$ . Compounds in which an element has a covalency of seven are very uncommon,  $\text{IF}_7$  (Ruff, 1930), being probably the only reliable example. Several salts are known in which there is an apparently odd covalency, but X-ray investigation of the crystal structure has shown that it is simply an effect of packing in the crystal, and that the co-ordination number is actually even (Powell and Wells, 1935). Cobalt apparently forms a five-covalent ion  $[\text{Co}(\text{CN})_5]'''$ , but its constitution is probably  $[\text{Co}(\text{CN})_5(\text{H}_2\text{O})]'''$  with a covalency of six.

### WAVE MECHANICS \*

In view of the fact that wave mechanics has already made, and is likely in the future to add further important contributions to chemistry, it is desirable for students of physical chemistry to have some acquaintance with the ideas underlying the subject. The actual application of the equations of wave mechanics to the

\* Wave mechanics is one aspect of a subject generalised under the title of quantum mechanics.



solution of problems involves high mathematical skill, and it is only possible here to give a very elementary and simplified outline of the methods used.

**Particles and Waves.** It is well known that many of the properties of light can only be explained by assuming it to consist of a train of waves, but if the gaps through which it passes or the obstacles it encounters are relatively large in comparison with the wavelength, the light may equally well be considered to be made up of a series of particles. In fact the quantum theory requires, from the point of view of energy at least, that light should have a corpuscular or discrete structure. In 1924 de Broglie suggested that matter and electrons, which had been always regarded as essentially of a discrete, or particle, nature, have also wave properties when in motion, and these have to be taken into consideration in the study of systems of atomic dimensions; the wavelength of the "material waves" was shown to be given by the equation  $\lambda = h/mv$ , where  $h$  is Planck's constant,  $m$  the mass of the particle and  $v$  its velocity. When Schrödinger (1926) gave this theory its mathematical development there was no experimental evidence that electrons or other particles were associated with waves in any manner, but shortly afterwards Davisson and Germer (1927) and G. P. Thomson (1928) found that a stream of electrons became diffracted and showed interference phenomena as a result of reflection at the surface of a single crystal or of passage through a thin film of matter; the postulation of wave properties thus became inevitable. Further confirmation of de Broglie's theory was obtained by calculating the wavelengths to be expected from his equation and comparing them with those found from the interference experiments; with electrons, for example, moving with a speed of  $10^9$  cm. per sec., the mass is  $1/1850$  that of the hydrogen atom ( $1.65 \times 10^{-24}$  gm.) and  $h$  is  $6.547 \times 10^{-27}$  erg-sec., and so  $\lambda$  should be  $0.75 \times 10^{-8}$  cm. It is for such waves that matter, with its atoms spaced at distances of the order of  $10^{-8}$  cm. apart, would act as a diffraction grating. Further experiments by Stern and Estermann (1930) have shown that atoms of hydrogen and helium show interference phenomena and so must have wave properties. The diffraction of electrons



and of matter has been studied to such an extent in recent years that there is now no doubt as to the facts.

Many attempts have been made to reconcile the wave and particle aspects of the electron; as in the case of light the two points of view are not mutually exclusive but complementary. The chemist, however, prefers to have a reasonably concrete picture by means of which the two aspects of the electron are made clear to him. Schrödinger, in his original development of the wave theory, preferred to regard the electron as "smeared out" into a cloud of electricity, and considered that the charge density in this cloud was determined by a wave equation, but this point of view is not essential, and it is just as satisfactory still to think of the electron as a particle with a wave function governing the probability of its occurrence at any point in space.

**The Schrödinger Equation.** The simple form of Schrödinger's wave equation, for a single particle, is of the same type as the equation representing the fluctuation of pressure at a point within a sound wave in three dimensions, thus

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0,$$

where  $\psi$  is a function of the space co-ordinates  $x$ ,  $y$  and  $z$ ,  $m$  is the mass of the particle,  $h$  is Planck's constant,  $V$  is the potential energy, which depends on  $x$ ,  $y$  and  $z$ , and  $E$  is a constant, being the total energy of the particle for a given value of the function  $\psi$ . For a hydrogen atom, with its one electron, the wave equation has the form given,  $m$  being the mass of the electron, and  $V$  is equal to  $-e^2/r$ , where  $e$  is the electronic charge and  $r$  the distance from electron to nucleus. In the wave equation for more complex atoms or molecules the terms involving the second differential of the function  $\psi$  are more complicated, involving  $\psi$  terms for each electron, and so also is the expression for the potential energy; it is not necessary for our purpose, however, to discuss the details. The method of solving differential equations of the type under discussion is familiar to mathematicians, and it is known that only for certain definite values of the energy quantity  $E$  are there corresponding forms of the function  $\psi$  which are finite, single



valued and continuous throughout space. It can be shown that  $\psi^2$  is related to the probability of the occurrence of an electron at any point with co-ordinates  $x$ ,  $y$  and  $z$ , and so it follows that only for particular values of the total energy  $E$  of the system will there be a definite function determining the presence of an electron in any position. These values of  $E$ , called the "eigenvalues," correspond therefore to the definite energy levels, or orbits, occupied by an electron in Bohr's original theory; the corresponding forms of  $\psi$  are termed the "eigenfunctions," or "wave functions." The wave function of an electron is the equivalent in terms of quantum mechanics of what has been generally called the electron orbit. For this reason the term "orbital" has come into common use (*vide infra*) as an alternative name for the wave function, especially in so far as it determines the probability of the electron being in a given place.

**Quantum Numbers.** In the complete solution of the differential wave equation for the hydrogen atom it is found that the eigenvalues of  $E$  are given by the equation

$$E_n = - \frac{2\pi^2 m_0 e^4}{n^2 h^2}.$$

where  $m_0$  is the mass of an electron,  $e$  its charge,  $h$  Planck's constant, and  $n$  an integer. This is identical with the equation, deduced by Bohr, for the amount of energy required to bring an electron from infinity to the  $n$ th orbit surrounding a hydrogen nucleus. It is clear, therefore, that the combination of the fundamental equation of the quantum theory, viz.,  $E' - E'' = h\nu$  (p. 6), with the solution of the Schrödinger wave equation, gives a formula for the frequencies of the lines of the hydrogen spectrum, apart from fine structure, identical with that of Bohr. The new theory thus gives the correct results without the necessity of the *arbitrary* assumptions made by Bohr that electrons can only move in certain orbits in which the angular momentum must be an integral multiple ( $n$ ) of  $h/2\pi$ ; the integral quantum numbers appear *automatically* in the wave mechanical solution as a consequence of the necessity for the wave functions  $\psi$  to be finite and continuous.



Further, the application of the Schrödinger equation to the problem of the possible energy states of a linear oscillator or of a rigid rotator with a free axis leads to results which are in better agreement with experimental observations of band spectra (Chapter IV.) than are those of the old quantum theory. In these and in other ways the theory of the association of a wave function with electrons, and with moving particles in general, has been amply justified.

## QUANTUM MECHANICS AND MOLECULAR STRUCTURE

The applications of the principles of quantum mechanics make it possible theoretically to write an equation for any system of nuclei and electrons, the solution of which would give complete information concerning the stability of the system and the arrangement of the nuclei in space. Theoretically, therefore, the problems of valency and of stereo-chemistry could be solved by the equations of wave mechanics, but unfortunately the complexities are so considerable that only in the very simplest cases, *e.g.*,  $H_2$  and  $H_2^+$ , has it been hitherto possible to integrate the appropriate Schrödinger equations with any degree of accuracy. Consequently the application of quantum mechanics to the subject of valency involves at the present time approximate treatment, and two methods of approach have been developed. It must be realised that both lines of attack are only approximate, but they often lead to results of the same nature, although the methods used are different: it is to be expected, of course, that as the approximations are diminished the conclusions reached should be identical in the two cases.

**The Heitler-London Method.** The first method of applying wave mechanics to the study of molecular structure was originally proposed by Heitler and London (1927), and is often designated as the Heitler-London method, although it has been extended in various ways, notably by Slater (1931) and Pauling (1931), and others, more recently. It is sometimes called variously the "homopolar method," for reasons which will appear shortly, the "method of localised (electron) pairs," or the "method of



valence-bond wave functions"; the two latter names are used especially in connection with its application to the study of the structure of polyatomic molecules. In the Heitler-London procedure it is assumed that the atomic wave-functions, or orbitals, of the electrons, these being defined as the wave functions for each electron moving in the field of only one atom, are known, and it is supposed that when the atoms combine to form a molecule these functions *remain unchanged*. The orbital part of the molecular wave-function is then constructed as the sum of the products of the atomic wave-functions. Consider, for example, a diatomic molecule AB, with two electrons which are of importance in the union of the atoms, then the wave function  $\Psi$  of the molecule, according to the Heitler-London approximation, is given by

$$\Psi = C \{ \psi_A(1)\psi_B(2) + \psi_A(2)\psi_B(1) \} \quad . \quad . \quad . \quad (i.)$$

where  $\psi_A$  and  $\psi_B$  are the atomic orbitals of the electrons designated (1) and (2), with reference to the atoms A and B, respectively. The factor  $C$  is introduced for "normalisation" purposes, in order to ensure that the total probability of the existence of any electron in the whole of space amounts to unity. It will be seen subsequently that an essential consequence of the wave-mechanical treatment is that there is another molecular wave-function involving the same terms as in equation (i.), but a minus sign replaces the plus between them: although this fact is of fundamental importance it need not be considered at the moment. Now that the molecular function is known, the energy of the molecule can be expressed in terms of a number of integrals which depend on its size and shape, but involving only atomic wave-functions. If the necessary integration is possible, which is not often the case, the energy of the molecule can be evaluated, but even if this cannot be done other information of importance can be obtained, as will be seen later.

**The Method of Molecular Orbitals.** The second method of attack is generally known as the "method of molecular orbitals," and has been developed by Lennard-Jones (1929), following Hund (1928), and particularly by Mulliken (1931 *et seq.*). A molecular orbital is defined as the wave function of an electron



as it moves in the field of all the other electrons and the nuclei constituting the molecule, and is generally expressed as a linear combination of atomic orbitals. This constitutes an essential difference between the molecular orbital method, and that of Heitler and London, in which the atomic orbitals are retained in the molecule. In the case of the substance AB already considered, the molecular orbitals of the two electrons may be taken as  $a\psi_A(1) + b\psi_B(1)$  and  $a\psi_A(2) + b\psi_B(2)$ , where  $\psi_A$  and  $\psi_B$  are, as before, the atomic orbitals, and  $a$  and  $b$  are the coefficients determining the extents to which the two atomic wave-functions take part in the molecular orbital; normalisation requirements make the sum of  $a^2$  and  $b^2$  practically equal to unity. The wave function of the molecule is then assumed to be expressed by the product of the separate molecular orbitals, so that

$$\begin{aligned}\Psi &= \{a\psi_A(1) + b\psi_B(1)\}\{a\psi_A(2) + b\psi_B(2)\} \\ &= a^2\{\psi_A(1)\psi_A(2)\} + b^2\{\psi_B(1)\psi_B(2)\} + \\ &\quad ab\{\psi_A(1)\psi_B(2) + \psi_A(2)\psi_B(1)\} \quad (\text{ii.})\end{aligned}$$

**Comparison of the Two Methods.** An examination of equation (i.) for the molecular wave-function given by the Heitler-London method, shows that it is virtually identical with the third term in equation (ii.), leaving two additional terms in the molecular-orbital treatment. It will be seen that each of these terms represents a condition in which both electrons (1) and (2) are on the same atom: in the first term they are both on the atom A and in the second term on the atom B. It follows, therefore, that these terms give the wave functions for the molecule in the ionic states  $A^-B^+$  and  $A^+B^-$ , respectively, and they are consequently called "ionic terms." It is the presence of these terms in the molecular-orbital treatment which differentiates it essentially from the Heitler-London method: this explains why the latter is sometimes called the "homopolar" method. If  $a$  is equal to  $b$  in equation (ii.), then the molecule may be supposed to spend equal times in the two possible ionic states, so the net result is that the molecule is non-polar, but if  $a$  and  $b$  are not equal the molecule has a polar structure. Although ionic states may well contribute to some



extent to the structure of many compounds, so that the Heitler-London method is incomplete, the weakness of the molecular-orbital procedure is that as a rule it exaggerates the effect of the ionic terms. For example, Van Vleck (1933) has calculated, if carbon and hydrogen are assumed to have the same ionisation potential, that the molecular-orbital treatment would require methane to spend 73 per cent. of its time in one or other of various ionic states and only 27 per cent. in the purely covalent form. This proportion appears to be quite incorrect, the ionic contribution being much too large.

**The Hydrogen Molecule.** One of the simplest and most complete applications of the wave-mechanical procedure to molecular structure is to the interaction of two hydrogen atoms to form a molecule. The treatment of Heitler and London (1927, 1928) may be explained as follows. The wave function of an electron in the ground state of a hydrogen atom is known in terms of its distance from the nucleus by the solution of the wave equation; this may be represented by  $\psi_a(1)$  for the electron associated with one hydrogen nucleus, and  $\psi_b(2)$  for the second electron associated with the other nucleus. A permissible structure of the molecule is then determined by the product of these atomic orbitals, thus  $\psi_a(1)\psi_b(2)$ , in which it is supposed that electron (1) is always on one of the hydrogen atoms, designated by  $a$ , and the electron (2) always on the other atom, represented by  $b$ . Quantum mechanics, however, does not permit of a distinction being made between the electrons (1) and (2), which are, of course, exactly similar, so that another possibility for the structure of the hydrogen molecule is represented by  $\psi_a(2)\psi_b(1)$ , in which the two electrons have changed places. According to the Heitler-London method of computation, the orbital part of the wave function of the hydrogen molecule is then a linear combination of the two products, both sum and difference being possible; thus

$$\Psi_S = \frac{1}{\sqrt{2 + 2T^2}} \{ \psi_a(1)\psi_b(2) + \psi_a(2)\psi_b(1) \} \quad . \quad . \quad (\text{iii.})$$

and 
$$\Psi_A = \frac{1}{\sqrt{2 - 2T^2}} \{ \psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1) \} \quad . \quad . \quad (\text{iv.})$$



where the quantity outside the bracket, involving the term  $T$ , is the normalisation factor in each case;  $T$  is a function only of the distance between the two hydrogen nuclei. The two alternative wave-functions, in the combined system of the two atoms, differ according to whether they are symmetrical or antisymmetrical in their co-ordinates: the symmetrical function  $\Psi_s$  is one which remains unaltered when the co-ordinates of the two electrons are interchanged, whereas the antisymmetrical function  $\Psi_A$  has its sign altered by a similar exchange. By means of the wave equations it is possible to calculate the total energy of the combined system of two hydrogen atoms for various distances apart in the two cases, that is with symmetrical and antisymmetrical orbital wave functions: these are represented by

$$E_s = 2E_H + \frac{Q + J}{1 + T^2} \cdot \cdot \cdot \cdot \cdot \cdot \quad (\text{v.})$$

and

$$E_A = 2E_H + \frac{Q - J}{1 - T^2} \cdot \cdot \cdot \cdot \cdot \cdot \quad (\text{vi.})$$

where  $2E_H$  is the energy of the two separate hydrogen atoms. The remainder of the energy is divided into two parts  $Q$  and  $J$ , both of which vary with the distance between the two nuclei: the quantity  $Q$  is called the Coulomb energy, as it is due to the "classical" electrostatic attraction between the electrons and protons and to the repulsion between the protons and between the electrons, whereas  $J$  is called the "exchange" or "resonance" energy, and results from the possibility of the electrons changing places in the hydrogen molecule. This exchange energy has no analogue in classical theory, and is an important consequence of the wave-mechanical treatment: without it the hydrogen molecule would apparently be very unstable. The two different energies,  $E_s$  and  $E_A$ , which result from the inclusion of the resonance, or exchange, effect is somewhat analogous to the phenomenon observed when two strings vibrating, or two pendulums swinging, at the same frequency are coupled together; the combined system can then vibrate with two new frequencies, one being greater and the other less than the original frequency of the uncoupled strings or pendulums.



The difference between  $E_S$  or  $E_A$ , the energy of the combined system of two hydrogen atoms and  $2E_H$ , the energy of the separated atoms, gives the binding energy, or potential energy, of the molecule, and this can be evaluated for various internuclear distances. Although the Coulomb energy can be determined accurately, only an approximate expression for the resonance energy was obtained by Heitler and London, which was subsequently evaluated

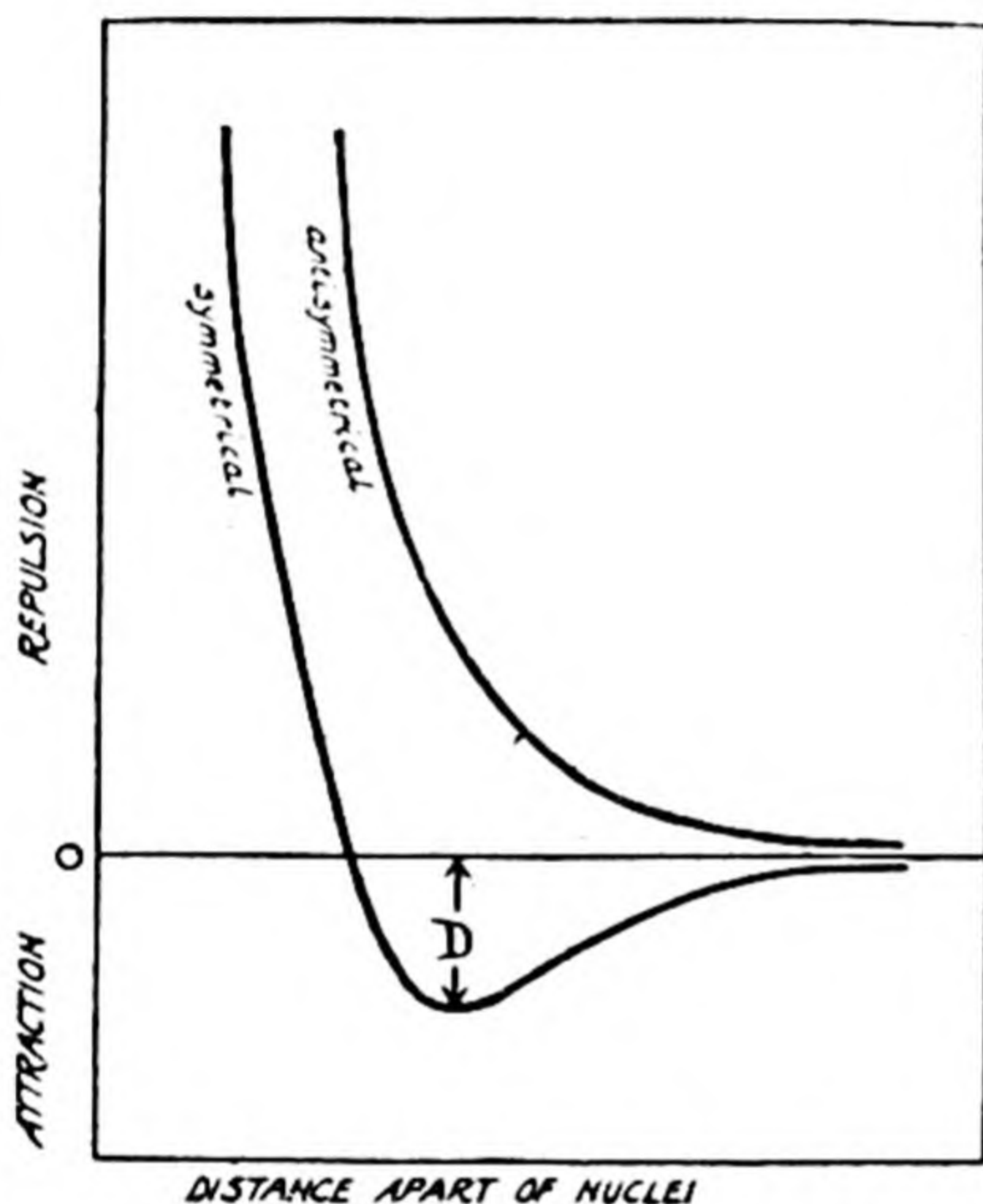


FIG. 1.—Variation of potential energy, with distance apart of nuclei, of a hydrogen molecule, having (a) symmetrical, (b) antisymmetrical, orbital functions. (After Heitler and London.)

by Sugiura (1927), and improved by Wang (1928), and by others, who introduced various corrections to which reference will be made shortly. The general form of the results is, however, quite definite and is shown diagrammatically in Fig. 1, in which the values of the potential energies,  $E_S - 2E_H$  and  $E_A - 2E_H$  have been plotted against the corresponding separation of the two hydrogen nuclei. For the antisymmetrical solution the curve shows that the energy of the combined atoms would always be greater than for the two separate atoms, represented by the zero line; this means that the molecule would immediately dissociate into its constituent atoms or, in other words, two hydrogen atoms for which the orbital portions of the molecular wave-functions are antisymmetrical would repel one another and to an increasing extent as they are brought closer together. When the orbital molecular wave-function is symmetrical, however, it can be seen from Fig. 1 that there is a range over which the energy of the combined atoms is less than when separated; the two atoms

by Sugiura (1927), and improved by Wang (1928), and by others, who introduced various corrections to which reference will be made shortly. The general form of the results is, however, quite definite and is shown diagrammatically in Fig. 1, in which the values of the potential energies,  $E_S - 2E_H$  and  $E_A - 2E_H$  have been plotted against the corresponding separation of the two hydrogen nuclei. For the antisymmetrical solution the curve shows that the energy of the combined atoms would always be greater than for the two separate atoms, represented



can then attract one another and a stable molecule will result, with the condition of maximum stability, that is, minimum potential energy, represented by the lowest point of the curve. The value of  $E_S - 2E_H$  at this point may be regarded as a measure of the energy required to separate the combined system into two separate atoms, and hence to the heat of dissociation ( $D$ ) of the hydrogen molecule. The distance apart of the hydrogen nuclei at the minimum point in Fig. 1 may be taken as giving the value in a normal molecule. In this manner the heat of dissociation and dimensions of the hydrogen molecule may be calculated from the equations of wave mechanics.

The earliest estimates were in error because of the neglect of several factors: allowance for the mutual shielding of the electrons from the nuclei was made by Wang (1928), who improved in this way on the original results of Sugiura (1927). Subsequently corrections were applied for the polarisation of one atom by the other (Rosen, 1931), and for the ionic terms, which should be involved to some extent but which, as already shown, are excluded by the Heitler-London approximation (Weinbaum, 1933). The most recent calculations by James and Coolidge (1933), who also allowed for the interaction between the two electrons, has given results for the heat of dissociation of hydrogen and for the internuclear distance which are in remarkable agreement with the observed values. Some of the more important data are recorded

TABLE XI.—*Constants for Hydrogen Molecule from Wave Mechanics*

Author.	Nuclear Distance ( $10^{-8}$ cm.)	Heat of Dissociation (cals./gm. mol.)
Sugiura . . . . .	0.80	66,300
Wang . . . . .	0.76	80,500
Rosen . . . . .	0.77	93,000
Weinbaum . . . . .	0.77	94,600
James and Coolidge . . . . .	0.74	103,000
Observed from spectra . . . . .	0.74	103,000



in Table XI., together with the values determined from spectroscopic measurements (see Chapter IV.). Allowance has been made in all cases for the zero-point energy of the hydrogen molecule (p. 217).

**Distribution of Charge Density.** The conclusion that  $\Psi_s$  leads to the formation of a stable molecule between two hydrogen atoms, whereas  $\Psi_A$  corresponds to a repulsive state can be seen in a qualitative manner by considering the distribution of charge density round the nuclei. The probability of the occurrence of the electrons at a point in the neighbourhood of the hydrogen nuclei may be taken as the square of the molecular wave-function, and this can be regarded as a measure of the charge density. Between the nuclei  $T$  is small in comparison with unity, and so equations (iii.) and (iv.) may be simplified so that it is possible to write

$$\Psi_s^2 = (A^2 + B^2 + 2AB)/2 \quad . \quad . \quad . \quad (vii.)$$

$$\Psi_A^2 = (A^2 + B^2 - 2AB)/2 \quad . \quad . \quad . \quad (viii.)$$

where  $A$  represents  $\psi_a(1)\psi_b(2)$  and  $B$  is written for  $\psi_a(2)\psi_b(1)$ . The electronic charge density between the nuclei must consequently be greater for the symmetrical function than for the antisymmetrical case, since  $A$  and  $B$  are positive. The presence of electrons between the hydrogen nuclei means that the latter are bound together to form a stable molecule, and this only occurs when the orbital part of the wave function is symmetrical. The same result is obtained more explicitly by plotting contours of equal charge density round the nuclei: it is found that whereas for the symmetrical wave-function the electrons tend to be shared between the nuclei, for the antisymmetrical function they each prefer to remain near their respective nuclei, which is equivalent to a system of two hydrogen atoms.

**States of Molecular Hydrogen.** In terms of wave mechanics the Pauli exclusion principle implies that in no atomic or molecular system can the *complete* wave-function of the system be symmetrical with respect to similar particles, electrons or nuclei. This complete function for an electron is the product of the orbital function, determining the probability of finding the electron at a given



point, *i.e.*,  $\Psi_S$  or  $\Psi_A$ , which has been already considered, and the spin function; the latter can only have one of two values corresponding to the spin quantum numbers of  $+\frac{1}{2}$  or  $-\frac{1}{2}$  (p. 8). If the two electrons in a hydrogen molecule have spins in the same direction, *i.e.*, parallel, then the spin function, which may be written as  $S_S$ , is symmetrical, since the sign of the function remains the same if the electrons are interchanged; if the spins are in opposite directions, *i.e.*, anti-parallel, however, the spin function  $S_A$  is antisymmetrical. There are thus four conceivable complete wave functions,

$$\Psi_S S_S, \Psi_S S_A, \Psi_A S_S \text{ and } \Psi_A S_A,$$

for the two electrons in the molecule of hydrogen; by the Pauli principle, however, only the antisymmetrical ones, namely,  $\Psi_S S_A$  and  $\Psi_A S_S$ , involving the product of one symmetrical and one antisymmetrical partial function, are possible. It has been seen from the work of Heitler and London described above, that only when the orbital part of the molecular wave-function is  $\Psi_S$ , that is, symmetrical, can a molecule of hydrogen be formed; hence it follows that two hydrogen atoms can combine to give a molecule only when the spin function is  $S_A$ , that is, when the two electrons have anti-parallel, or oppositely directed, spins. The resultant electron spin of the stable molecule is consequently the sum of  $+\frac{1}{2}$  and  $-\frac{1}{2}$ , that is zero. The repulsive state with the antisymmetrical orbital function is only possible when the spin function is symmetrical: the resultant spin of this system is consequently the sum of  $+\frac{1}{2}$  and  $+\frac{1}{2}$ , that is unity.

Since the quantum number  $\Lambda$  for the component of the resultant orbital angular momentum for a combination of two hydrogen atoms must be zero (see p. 11), both stable and repulsive states of the hydrogen molecule postulated by the Heitler-London theory are to be represented as  $\Sigma$  states. The resultant spin quantum numbers, as shown above, are 0 and 1, respectively, and consequently the stable hydrogen molecule should be  $^1\Sigma$  in the ground state, whereas a  $^3\Sigma$  state should be unstable. This is in agreement with the experimental results obtained from a study of the molecular spectra, there being evidence that the unstable



$^3\Sigma$  state is concerned in the formation of certain continuous spectra. It will be seen in Chapter IV. that such bands imply that the molecule dissociates into atoms, a result to be expected if the  $^3\Sigma$  state is involved. The existence of these spectra shows, incidentally, that the unstable, repulsive state has some physical reality.

**The Heitler-London Theory of Covalency.** Although G. N. Lewis was led to suggest that a pair of electrons, rather than a single electron, represents a valency bond by the empirical fact that the vast majority of actual compounds contain an even number of electrons, it now appears that there may be theoretical basis underlying this concept. The formation of a stable molecule of hydrogen can only occur by the coupling of two electrons with opposite spins, and consequently an electron-pair of this kind would appear to be the fundamental unit of chemical union. Although such a view is not universally accepted (p. 86) it has been made the basis of a general theory of covalency by Heitler and London. The covalency of any element *due to the sharing of electrons*, and not including semi-polar bonds, will be equal, according to this theory, to the number of *unpaired* electron spins in the atom: in chemical combination it is supposed that there is a tendency for the electrons to be coupled with those of other atoms having opposite spins. In fluorine, for example, there are seven electrons in the second quantum group; according to the Pauli principle these electrons must fall into four groups of two electrons with opposite spins in each, and so it follows that six of the spins must be paired in three of the sub-groups and the fourth contains one electron with an unpaired spin. Fluorine should thus be univalent. Similarly oxygen may have 0 or 2 unpaired spins, nitrogen 1 or 3, and carbon 0, 2 or 4; the normal valencies can be accounted for in this manner.

**Valency and Spectral Multiplicity.** It has been already seen (p. 11) that the multiplicity  $M$  of any line in the spectrum of an atom is equal to  $2S + 1$ , where  $S$  is the resultant spin quantum number. Electrons with paired spins ( $+\frac{1}{2}$  and  $-\frac{1}{2}$ ) contribute nothing to the value of  $S$ , which is consequently the sum of the unpaired spins; since the latter each have a value of  $\frac{1}{2}$ , it is clear



that  $2S$  gives the number of electrons in the atom with unpaired spins. According to the Heitler-London theory the numerical value of the covalency is determined by the unpaired spins, and so it follows that the valency  $V$  is given by the relationship

$$V = M - 1 \dots \dots \dots (ix.)$$

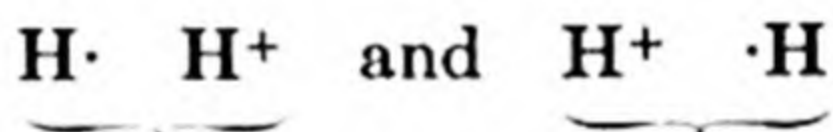
The nitrogen atom in its ground state has a  $4S$  term, and so its shared covalency should be 3, in agreement with its chemical behaviour. The normal state of the carbon atom is  $3P$ , with two  $p$  electrons having uncoupled spins; the covalency should, therefore, be 2, although it rarely has this value. It must be assumed, therefore, that as a general rule carbon probably enters an "excited" state before taking part in chemical combination. Until recently it was believed that this was the spectroscopically known  $5S$  state, with four electrons uncoupled (p. 10), and the energy difference between it and the ground level was thought to be about 1.6 electron-volts, that is about 37,000 cal. per gm. mol., which is not very considerable. Van Vleck (1934) has shown, however, that the  $5S$  state involved in the atomic spectra of carbon is actually 4.3 electron-volts above the ground state, but this is not concerned in the formation of quadrivalent compounds; the actual excited state which takes part in chemical combination is believed to have a still higher energy, namely 7 electron-volts, or about 161,000 cal. per gm. mol. When another atom is brought up to the normal carbon atom the latter must gradually acquire this energy, which amounts to approximately 40,000 cal. per bond; although this appears very large, it is not impossible when it is remembered that the energy liberated in the formation of a single bond with a carbon atom may be of the order of 70,000 to 90,000 cal. (see p. 253). Part of the energy of combination is evidently used up in raising the carbon atom to the excited state in which it has four electrons with uncoupled spins, and is effectively quadrivalent. The connection between electron spin and covalency is of great interest; it has certainly opened up a new aspect of the subject, and has provided some justification for the electron duplet as the unit of chemical bonding. It is, however, not the only theory of valency resulting from the



application of wave mechanics : the consequences of the alternative treatment by the method of molecular orbitals will be considered later.

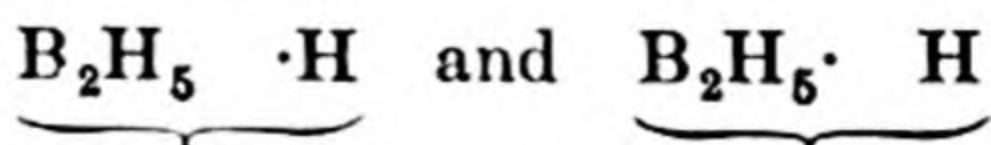
### ODD-ELECTRON LINKAGES

**One-Electron Bonds.** Application of the methods of wave mechanics, as described above in connection with the hydrogen molecule, has also been made to the hydrogen-molecule ion,  $\text{H}_2^+$ , and it has been found that because of the inclusion of exchange energy the ion is quite stable, in spite of the fact that there is only one electron to hold the two hydrogen nuclei together. The first approximate calculations of the dissociation energy were made by Burrau (1927), and more accurate treatments have been devised by others (*e.g.*, Jaffé, 1934) : the calculated value is in excellent agreement with that obtained from spectroscopic data, namely about 60,000 cal. This surprisingly high amount is due almost entirely to the exchange energy, which may be ascribed to the fact that two equivalent states of the hydrogen-molecule ion are possible, thus



The correct wave functions for the molecule are then the sum and difference of the functions for the two separate structures : the former of these functions, as in the case of the hydrogen molecule, corresponds to the stable combination.

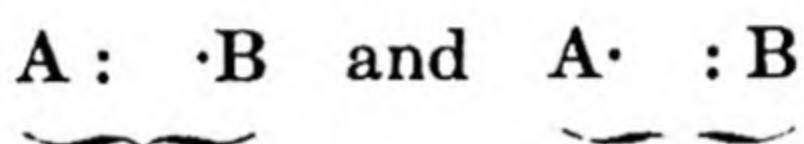
Pauling (1931) has extended this idea of one electron being able to hold two atoms together as a result of the exchange effect, and has postulated that such one-electron bonds, that is singlet linkages, are possible when there are two conceivable electronic states with essentially the same energy ; this occurs especially when the two atoms joined by the single electron are identical, as in  $\text{H}_2^+$  and the hypothetical  $\text{Li}_2^+$  and  $\text{Na}_2^+$ , or closely similar. It has been already mentioned (p. 31) that in the boron hydride  $\text{B}_2\text{H}_6$  it seems impossible to avoid the necessity for including singlet linkages, and Pauling suggests that there is reason for believing that the two electronic states





have similar energies, so that a single electron is able to hold the hydrogen atom to the boron, as a result of the exchange effect. This is another example of the important phenomenon of "resonance," which is considered in some detail later. It follows also that additional stability, due to resonance, results from the fact that a number of different electronic structures, having identical energies, are possible resulting from an interchange of the hydrogen atoms attached to the boron by the single electrons.

**Three-Electron Bonds.** The concept of the one-electron bond has been extended by Pauling to include three-electron linkages; these may be formed when two configurations of the compound AB, viz.,



correspond to the same energy. In such a case stabilisation of the three-electron bond, as a result of exchange, or resonance, energy is possible. The remarkable fact that nitric oxide, with its odd number of electrons, shows no tendency to form  $N_2O_2$  is accounted for by the presence of a three-electron bond, in addition to two normal duplets, thus



Since the nitrogen and oxygen nuclei are so similar it is not difficult to believe that the two forms, resulting from electron exchange, will have similar energies. A structure of the same type is suggested for nitrogen dioxide, one oxygen atom being attached by a pair of electron-duplets and the other by a duplet and a triplet.

In order to account for the heats of dissociation of these molecules it is necessary to suppose that the single- and triple-electron bonds each have about half the strength of a normal duplet-bond. This and other aspects of the subject will be considered later from the point of view of molecular orbitals (p. 86).



**WAVE MECHANICS AND MOLECULAR CONFIGURATION**

The method of "valence-bond wave functions," as first developed independently by Slater (1931) and Pauling (1931), is an important application of the Heitler-London principle of the electron-pair bond which has given results of importance to chemistry. Starting with the idea that a chemical linkage is formed by the coupling of two electrons having opposed spins, one from each atom involved in the union, it is postulated that the direction in which the orbital molecular wave-function is a maximum will represent the direction of the valency bond formed by the particular atom originally owning the electron under consideration. The value of the function, under analogous conditions, may be taken as approximately proportional to the strength of the linkage. Since the wave function is related to the probability of finding an electron at a given point (p. 56), it is reasonable to assume that a valency bond will operate in the direction in which the electron is most likely to be found.

**Valency Angles.** If an *s* electron (see p. 7), as in the hydrogen atom, is available for forming a linkage then the wave function will be spherically symmetrical about the nucleus, as might have been anticipated; according to Pauling the value is then 1.0. When *p* electrons take part in bond formation the maximum values of the orbital functions are found to be  $\sqrt{3}$ , in directions at right angles to one another; bonds formed with *p* electrons are thus supposed to be stronger than those formed with *s* electrons having the same principal quantum number. An interesting application of these results is to the normal oxygen atom which has two unpaired *p* electrons; when oxygen unites with hydrogen the angle between the linkages should be  $90^\circ$ , or perhaps slightly more because of the mutual repulsion of the hydrogen atoms (see also p. 74). It will be seen later (Chapter III.) that there is strong evidence for an angular, rather than a linear, structure for the water molecule; the actual angle has been assessed from spectroscopic data (Mecke, 1932) as about  $106^\circ$ . The structure of sulphuretted hydrogen should be similar to that of water, and various lines of physical evidence lead to a valency angle of about  $90^\circ$  for its



sulphur atom (Dadieu and Kohlrausch, 1932 ; Cross, 1934). The normal atom of nitrogen contains three unpaired  $p$  electrons, and so it should form three bonds at right angles to one another ; a pyramidal structure should consequently result for ammonia and its derivatives. Such an arrangement is in general agreement with the results of the determination of dipole moments (Chapter III.) and of molecular spectra (Chapter IV.), although it appears that the angle between the valency bonds is somewhat greater than  $90^\circ$ .

**Tetrahedral Carbon.** It has been already stated that the carbon atom becomes quadrivalent in an excited state (p. 67) ; it then has one  $s$  and three  $p$  electrons with unpaired spins. At first sight it might be expected that wave mechanics would lead to the conclusion that the latter should form three linkages at right angles, with strengths proportional to  $\sqrt{3}$ , and the  $s$  electron should form a different type of weaker linkage with strength 1.0 ; this is, of course, not the case. There is reason to believe that when the bond energy exceeds greatly the excitation energy required to raise an electron from the  $s$  to the  $p$  level—approximately 200,000 cal. per gm. atom for elements of low atomic weight—the quantisation is changed so that the  $s$  and  $p$  electrons all have equivalent wave-functions. This process is sometimes called  $sp$  hybridisation. The bond energy is generally of the order of 100,000 cal. per linkage, and so for carbon, which is quadrivalent, the total bond energy greatly exceeds the excitation energy and the condition for four equivalent orbital functions is realised. Calculation, by the methods of wave mechanics, shows that these four functions all have a maximum value of 2.0 in the directions of the corners of a regular tetrahedron, *i.e.*,  $109^\circ 28'$  apart ; this is in exact agreement with the views long held by chemists concerning the valency directions of the carbon atom.

In the quadrivalent, positively charged nitrogen atom there are also one  $s$  and three  $p$  electrons, and the conditions exist, as in carbon, for the formation of four equivalent wave-functions by hybridisation ; these again should have their maxima in directions making angles of  $109^\circ 28'$  with one another. Phosphorus in phosphonium compounds and boron in  $B_2H_6$  should have similar



configurations. Tervalent nitrogen with a bond energy of 300,000 cal. and an excitation energy of about 400,000 cal., for two electrons, is a border-line case, and Pauling considers that the valency angle in ammonia or amines may approach the tetrahedral value. As far as the former is concerned, the evidence from spectroscopic data confirms this view.

An important criticism of the Slater-Pauling hypothesis that the quantisation of an  $s$  electron may be changed in carbon compounds has been made by G. N. Lewis (1933) from a consideration of the series: methane, ammonia, water, hydrogen fluoride and neon, in all of which the electron octet is complete. Presumably the stability of the octet in every case is connected with the fact that it corresponds to the inert gas structure; in ammonia, water, hydrogen fluoride and neon two of the electrons will be in the  $s$  level and the other six will be  $p$  electrons, but if the four electron functions in carbon are equivalent this arrangement cannot apply to methane. Further, the suggestion that the ammonium ion has the same structure would imply a change of quantisation of the two  $s$  electrons when ammonia becomes an ammonium ion; this view seems difficult to accept. These difficulties do not arise to the same extent in the application of the concept of molecular orbitals, although the results are not so precise from the point of view of the chemist (*vide infra*).

**Co-ordination Compounds.** With atoms of high atomic weight in addition to  $s$  and  $p$  electrons some in the  $d$  level become available; if hybridisation occurs then nine wave functions are possible, but these cannot all be equivalent; since the co-ordination numbers of four and six are the most common these numbers of equivalent functions are the most interesting. If only one  $d$  electron is available then four equivalent bonds can be formed with one  $s$  and two  $p$  electrons, the maximum wave-functions (2.694) being at *right angles* to one another; this is found to be the case in the ions  $\text{Ni}(\text{CN})_4^{2-}$ ,  $\text{PtCl}_4^{2-}$ ,  $\text{PdCl}_4^{2-}$  and  $\text{AuCl}_4^-$ , which are known, from X-ray and other data, to have a planar structure. Pauling has pointed out that although the same elements give positive ions, *e.g.*,  $\text{Ni}^{2+}$ , which are definitely paramagnetic, the ions referred to as being planar should be diamagnetic on account of



the change in the quantisation of the electrons ; this has been found to be the case with  $\text{K}_2\text{Ni}(\text{CN})_4$  and  $\text{K}_2\text{Pt}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ . In the course of an investigation of magnetic properties of nickel complexes Sugden (1932) found the glyoximes of nickel to be diamagnetic ; in accordance with Pauling's theory they should, therefore, have a planar structure. If this is the case then unsymmetrical glyoximes of nickel should exist in two stereoisomeric configurations, and Sugden (1932, 1935) has actually isolated two forms of methyl-*n*-propyl-, -*n*-butyl- and -benzyl-glyoximes. It is possible that the isomerism may be due to the oxime existing in syn- and anti-forms, but from an examination of the substances this explanation appears improbable and the planar configuration is regarded as the cause of the isomerism.

When two *d* electrons with unpaired spins are available then six equivalent wave-functions can be formed by their combination with one *s* and three *p* electrons ; the maximum value of these functions is 2.923 directed towards the corners of a regular octahedron. This is the type of structure proposed by Werner to account for the optical isomerism in co-ordination compounds, and since accepted by most chemists to represent groups of the type of  $\text{Co}(\text{NH}_3)_6^{+++}$ ,  $\text{PtCl}_6^{--}$  and  $\text{Fe}(\text{CN})_6^{--}$ . Pauling (1932) considers that an alternative arrangement of six equivalent bonds, of strength 2.983, is possible in directions towards the corner of a triangular prism ;  $\text{MoS}_2$  is believed to have this type of structure in the crystalline form, but the matter seems very uncertain and further experimental evidence, particularly in connection with other molybdenum compounds, is required.

Finally, if three *d* electrons can take part in the formation of valency bonds because of their unpaired spins then four equivalent bonds, with strength 2.95, arranged *tetrahedrally* will result. This is apparently the case with the ions  $\text{CrO}_4^{--}$  and  $\text{MoO}_4^{--}$ , as well as with the complex cyanide ions  $\text{Zn}(\text{CN})_4^{--}$ ,  $\text{Cd}(\text{CN})_4^{--}$  and  $\text{Hg}(\text{CN})_4^{--}$ . The latter are known to have a tetrahedral structure from X-ray examination, and it is significant that the elements zinc, cadmium and mercury each have two *d* electrons more than nickel, palladium and platinum respectively. With the last three elements only one *d* electron is available for valency purposes, and a planar structure



results for the co-ordination number of four, but in the former three elements the two additional *d* electrons make a tetrahedral grouping more stable. It should be noted in conclusion that the large values of the electron wave-functions, 2.6—2.9, in the co-ordination compounds, as compared with 2.0 for carbon and 1.73 for oxygen, may account for the high degree of stability of these compounds.

**Molecular Configurations.** Another aspect of the Heitler-London-Slater-Pauling method, based on the principle of the electron-pair bond, is the direct application to a particular compound in order to determine its configuration, as a further development of the general question of valency angles already considered. By assuming that every bond consists of a definite localised pair of electrons, it is possible to write an expression for the potential energy *W* of the system in the form

$$W = Q + \Sigma_i J_{ii} - \frac{1}{2} \Sigma_{ij} J_{ij} \quad . \quad . \quad . \quad . \quad . \quad . \quad (x.)$$

where *Q* is the Coulomb energy and the *J* terms represent the exchange integrals; both *Q* and *J* involve the wave functions of the electrons and so are dependent on the shape of the molecule. The suffixes *ii* and *ij* are used to indicate that in the first case the exchange energy refers to the pair of electrons *ii* coupled in a definite bond, and the second to the energy between electrons *i* and *j* which are not paired together in this way. The potential energy of a given molecule can then be written down, assuming that the pairs of electrons making up the bonds are localised in definite positions corresponding to the direction of the valency bond. It is apparent that the value of the energy will depend on the configuration of the molecule, that is to say on the directions of the bonds, and the particular arrangement which leads to a minimum in the potential energy can be regarded as the most stable configuration.

The method has been applied to an examination of the H<sub>2</sub>O molecule, and it has been found that the two O—H bonds should make an angle of 90° with one another, in agreement with the conclusions already mentioned (p. 70), although an increase to 100° is to be expected as a result of repulsion between the hydrogen



atoms (Van Vleck and Cross, 1934). The actual value of  $106^\circ$  has been attributed to a tendency towards  $sp^2$  hybridisation in the oxygen atom, but it must be admitted that in any case the calculations are far from complete. The energy required to dissociate a molecule of water into its atoms has been estimated, by a method analogous to that used in connection with hydrogen, and the best value obtained so far is 130,000 cal. per gm. mol. (Coolidge, 1932), which is to be compared with the actual heat of dissociation of about 220,000 cal. The structure of ethylene has been investigated by the method of localised pairs, and it is concluded that the six nuclei, two of carbon and four of hydrogen, are all in one plane, and that the H—C—H angle is about  $130^\circ$  (Penney, 1934); this value is considerably larger than that generally assumed by chemists. Penney and Sutherland (1934) have used the same procedure to study the configuration of hydrogen peroxide and of hydrazine, and have shown that in neither case is there free rotation about the central bond, O—O or N—N, respectively, as might have been anticipated. Neither are the atoms all in one plane, for the minimum potential energy is given by an arrangement in which the azimuth of one-half of each molecule makes an angle of  $90^\circ$  to  $100^\circ$  with that of the other. The oxygen valency angle in hydrogen peroxide appears to be about  $100^\circ$ , a value close to that found for the water molecule. It should be noted that these results are in excellent harmony with observations of the dipole moments of water and hydrazine (Chapter III.), which had previously not been explained in a satisfactory manner. Mention may also be made of the proof, based on the concept of directed wave-functions and the electron-pair bond, that benzene is the most stable of any single-ring structure having the general formula  $(CH)_n$ , and that cyclo-octatetrene,  $C_8H_8$ , is the next in order of stability (Penney, 1934); the latter ring will not be planar like that of benzene. Further reference to the method of localised pairs will be made later.

### METHOD OF MOLECULAR ORBITALS

**The Hydrogen Molecule.** Although many of the developments of the method of molecular orbitals have been along different



lines to those discussed above in connection with the concept of localised pairs, in many cases the two procedures have been applied to an examination of the same problem, and some of these instances will be considered first. The stability of the hydrogen molecule has been treated by the method of molecular orbitals in the following manner. The molecular orbitals for each electron may be written in the form (see p. 59) :

$$\psi_g(1) = \frac{\psi_a(1) + \psi_b(1)}{\sqrt{2 + 2T}} \quad \dots \quad \text{(xi.)}$$

and 
$$\psi_u(1) = \frac{\psi_a(1) - \psi_b(1)}{\sqrt{2 - 2T}} \quad \dots \quad \text{(xii.)}$$

for electron (1), similar equations applying to electron (2). The  $\psi_a$  and  $\psi_b$  terms represent the ordinary atomic wave-functions (orbitals) for the electrons in the ground state of the two hydrogen atoms. The suffixes  $g$  and  $u$ , which are abbreviations for the German words "gerade" (even) and "ungerade" (odd), respectively, have the following significance: if on reflection of the co-ordinates of an electron in the mid-point of the internuclear axis the sign of the wave function remains unchanged, the electron is said to be in a  $g$  orbit, but if the sign changes the electron is in a  $u$  orbit. The electrons in the system consisting of two combined hydrogen atoms can have two possible states, represented by the  $g$  and  $u$  functions, in equations (xi.) and (xii.). For each of the electrons (1) and (2), two orbitals are possible, and these may be written  $\psi_g(1)$  and  $\psi_u(1)$ , and  $\psi_g(2)$  and  $\psi_u(2)$ , respectively. The orbital portion of the complete wave-function of the molecule, as already shown, is taken as the product of the individual molecular orbitals, modified as required by the exchange effect, and so four cases are possible, viz.,

- (i.)  $\Psi_1 = \psi_g(1) \psi_g(2) \quad \dots \quad 1\Sigma$
- (ii.)  $\Psi_2 = \psi_u(1) \psi_u(2) \quad \dots \quad 1\Sigma$
- (iii.)  $\Psi_3 = \{\psi_u(1) \psi_g(2) + \psi_u(2) \psi_g(1)\} / \sqrt{2} \quad \dots \quad 1\Sigma$
- (iv.)  $\Psi_4 = \{\psi_u(1) \psi_g(2) - \psi_u(2) \psi_g(1)\} / \sqrt{2} \quad \dots \quad 3\Sigma$

If both electrons are in the same type of orbit, either  $g$  or  $u$ , that



is for cases (i.) and (ii.), the Pauli principle requires their spins to be anti-parallel,  $+\frac{1}{2}$  and  $-\frac{1}{2}$ , so that the resultant spin is zero and the systems are in  $^1\Sigma$  states. When the electrons are in orbits of different types, as in cases (ii.) and (iii.), then the spins can be either anti-parallel, when the resultant is zero, or parallel, when it is unity: the symmetrical orbital combination (iii.) corresponds to the former case, and the antisymmetrical function (iv.) to the latter. Since they are both  $\Sigma$  states, the  $l$  values for the hydrogen atoms being zero (p. 8), case (iii.) represents a  $^1\Sigma$  and case (iv.) a  $^3\Sigma$  state.

It now remains to decide which of the four possibilities represents the conditions for a stable molecule: this can be done in an approximate, qualitative manner by considering the electronic charge distribution as determined by the square of the wave functions of the molecule, as already described (p. 64). Substituting the values for  $\psi_g$  and  $\psi_u$  from equations (xi.) and (xii.) into the various wave functions for cases (i.) to (iv.), and evaluating the squares, it is seen that case (i.) is the only one for which there is no term with a negative sign: it follows, therefore, that this corresponds to the maximum concentration of electrons between the nuclei and consequently to a stable molecule. The potential-energy curve for case (i.) is of exactly the same form as that for the symmetrical wave-function in Fig. 1, and the minimum, representing the equilibrium state of molecular hydrogen, is at an internuclear distance of  $0.73\text{\AA}$ ., compared with the experimental value of  $0.74\text{\AA}$ . The heat of dissociation has been calculated as 73,800 cal. per gm. mol., which is to be compared with the 80,500 cal. obtained by Wang (Table XI.) using the Heitler-London treatment. It is evident that although the extreme molecular-orbital treatment gives results of the correct order, as far as the hydrogen molecule is concerned it is not so good as the extreme atomic-orbital (homopolar) procedure. It may be pointed out that in case (i.), which represents the formation of a stable hydrogen molecule, two atoms having electrons with  $g$  orbitals and with anti-parallel spins combine: this is in agreement with the results obtained by means of the Heitler-London treatment.



**Ionic States of Hydrogen.** It will be observed that whereas the homopolar method postulates the possibility of only two states of the system involving two hydrogen atoms, the molecular-orbital treatment suggests that four are theoretically conceivable. By inserting the values of  $\psi_g$  and  $\psi_u$ , from equations (xi.) and (xii.) and multiplying out the wave functions for the hydrogen molecule in the four cases, the following results are obtained :

$$\Psi_1 = \frac{1}{2 + 2T} \{ \psi_a(1) \psi_b(2) + \psi_a(2) \psi_b(1) + \psi_a(1) \psi_a(2) + \psi_b(1) \psi_b(2) \} \quad . \quad . \quad . \quad \text{(xiii.)}$$

$$\Psi_2 = \frac{1}{2 - 2T} \{ - \psi_a(1) \psi_b(2) - \psi_a(2) \psi_b(1) + \psi_a(1) \psi_a(2) + \psi_b(1) \psi_b(2) \} \quad . \quad . \quad . \quad \text{(xiv.)}$$

$$\Psi_3 = \frac{1}{\sqrt{2 - 2T^2}} \{ \psi_a(1) \psi_a(2) - \psi_b(1) \psi_b(2) \} \quad . \quad . \quad . \quad \text{(xv.)}$$

$$\Psi_4 = \frac{1}{\sqrt{2 - 2T^2}} \{ \psi_a(1) \psi_b(2) - \psi_a(2) \psi_b(1) \} \quad . \quad . \quad . \quad \text{(xvi.)}$$

Comparing these equations with equations (iii.) and (iv.) for the molecular wave-functions given by the Heitler-London method, it is seen that  $\Psi_4$  of the latter is identical with  $\Psi_4$ ;  $\Psi_5$  corresponds with  $\Psi_1$ , as is to be expected since they both represent the stable  $^1\Sigma$  state of molecular hydrogen, except that, apart from a difference in the "normalisation" factor, the  $\Psi_1$  function contains two ionic terms representing conditions in which both electrons (1) and (2) are either on atom (a) or on atom (b); these are, of course, not included in the Heitler-London treatment. The functions  $\Psi_2$  and  $\Psi_3$  are characteristic of the molecular-orbital procedure only, and the reason is not difficult to find:  $\Psi_3$  in equation (xv.) consists of ionic terms exclusively, whereas in  $\Psi_2$  the ionic terms are the most important, since the function as a whole must be positive and the non-ionic terms in equation (xiv.) are preceded by a minus sign.

**Molecular Structure.** Although the method of molecular orbitals does not postulate the existence of definite bonding pairs



of electrons, it can nevertheless be applied to the study of molecular configuration, by evaluating the potential energy and determining the particular arrangement of atomic nuclei required to give the minimum value. The molecules of methane (Van Vleck, 1933), of ethylene (Penney, 1934), and of water (Van Vleck, 1935), amongst others, have been treated in this manner, and the conclusions reached are the same as those arrived at by the method of localised bonds. It appears that the tetrahedral arrangement in methane is explained without the necessity for postulating  $sp^3$  hybridisation (p. 71), but, on the other hand, it is admitted that it is not easy to account for the fact that  $\text{CH}_6$  does not exist! The alternative square or tetrahedral arrangements for four-covalent compounds, and the octahedral configuration for those having a co-ordination number of six, also follow from the concept of molecular orbitals (Mulliken, 1933; Van Vleck, 1933). If possible both procedures should be employed to study any particular problem, and if the conclusions reached are the same then the results may be accepted with some confidence.

**Electronic Configurations.** Another aspect of the molecular-orbital treatment, which is qualitative rather than quantitative, leads to results of considerable interest. So far little progress has been made for molecules containing more than two atoms, and so the discussion here will be restricted to diatomic compounds. Before considering some of these it will be convenient to explain the nomenclature, introduced by Mulliken, which is commonly used in this work to describe the electronic configurations of molecules. The method of representation employed for a molecule approaching the "united atom" state has been already described (p. 11), and in this it is supposed that the significance of the  $n$  and  $l$  quantum numbers is retained. When the constituent nuclei are drawn apart to form an actual molecule these numbers lose their precise meaning, although two equivalent quantum numbers of some kind must be used to describe the state of an electron. In order to show that such numbers exist, although their nature is generally not known, the integers and letters, viz.,  $1s$ ,  $2p$ , etc., used for the  $n$  and  $l$  quantum numbers,



are replaced by a letter near the end of the alphabet, *e.g.*,  $v$ ,  $w$ ,  $x$ ,  $y$  and  $z$ , each of which really stands for two quantum numbers. The more firm the binding of the electron the nearer is the letter to the end; thus a  $z$  electron is bound more firmly than a  $y$ , and a  $y$  more firmly than an  $x$  electron, and so on. These letters are now combined with the  $\sigma$ ,  $\pi$  and  $\delta$  symbols, which have the same significance as before (p. 11), to describe the molecular orbital of each electron in the molecule. One simplification which is generally used may be mentioned: the two  $s$  electrons in the first quantum group, described as  $1s^2$ , are so firmly bound that, except for hydrogen, they take no part in molecule formation. In a diatomic molecule there are, of course, two such electron-pairs, and they are represented by the symbol  $KK$ , the letter  $K$  being used to describe the first quantum group in X-ray notation. Electrons of this type, which do not influence the binding between atoms, may be regarded as retaining their atomic orbitals even in the molecule.

Since the  $1s$  level can be ignored, the  $2s$  level next comes up for consideration. There are two of these levels, one for each atom, and each contains two electrons previously designated as  $2s\sigma^2$ . By the Pauli principle there cannot be more than two  $\sigma$  electrons (p. 11) for any value of the two quantum numbers included in the letter  $x$ ,  $y$  or  $z$ , and so the two pairs must have different letters ascribed to them. In the molecule, Mulliken's nomenclature is  $(z\sigma)^2$  for one pair of molecular orbitals, and  $(y\sigma)^2$  for the other, in the order of decreased binding strength. A consideration of the molecular wave-functions arising from  $2s$  atomic orbitals shows that one electron is more firmly bound than the other, and so the division into the  $y$  and  $z$  groups is justifiable. The maximum number of possible  $2p$  orbitals for any atom is 6, and these are designated as  $2p\sigma^2$  and  $2p\pi^4$ : hence for a diatomic molecule there are two  $\sigma^2$  groups and two  $\pi^4$  groups, which are described by the notation  $(u\sigma)^2$  and  $(y\sigma)^2$ , and  $(v\pi)^4$  and  $(x\pi)^4$ , respectively, one pair in each case being more firmly held than the other. From various considerations, partly theoretical and partly empirical, based on data obtained from band spectra, Mulliken, following Hund and Lennard-Jones, has arranged the seven types of molecular orbital



already mentioned in the order of decreasing strength of binding to the nuclei, thus

$$K, z\sigma, y\sigma, x\sigma, w\pi, v\pi, u\sigma.$$

**The Nitrogen Molecule.** In developing the orbital configuration of a molecule it is supposed that the electrons are added one by one until all the orbital groups, starting from the most firmly bound, are gradually filled up. In view of the fact that a molecular orbital of a given electron is essentially the resultant of the influence of the nuclei and of all the other electrons, the order in which the groups are filled is not invariably the same, but for the present purpose it is sufficient to assume that it is always as given above. Consider as an example the formation of a molecule from two normal nitrogen atoms in the  $^4S$  state, having the configuration  $1s^2 2s^2 2p^3$ : the fourteen molecular orbitals, in six groups, are then arranged thus:

$$KK(z\sigma)^2(y\sigma)^2(x\sigma)^2(w\pi)^4.$$

Since all six groups are complete, the values of  $S$  and  $A$  are both zero (p. 11), and so the molecule is in a  $^1\Sigma$  state.

**Bonding and Anti-Bonding Electrons.** Consideration of the nitrogen molecule brings to light another important aspect of the orbital theory as applied to molecular structure. As part of what is known as the "aufbauprinzip" or "configuration theory," Mulliken has drawn up a chart showing the relationships between the orbital of an electron in the initial atomic state, in the molecule and in the united atom. In the latter the maximum number of quantum levels is obviously less than the total available in the initial atoms, consequently it frequently occurs that an electron from a given level in the single atom has to be ascribed to a higher level in the united atom. Some examples of the connection between the various orbitals, for a homonuclear molecule, are given on p. 82. The  $y\sigma$ ,  $x\sigma$ ,  $v\pi$  and  $u\sigma$  electrons are said to be "promoted," since their principal quantum number is higher in the united atom than it was initially. The act of promotion requires a large amount of energy, and consequently the presence of promoted electrons tends generally towards instability of the molecule: under these circumstances such electrons are consequently



termed "anti-bonding." These electrons are, however, not always anti-bonding; if in the actual molecule the nuclei are relatively far apart, so that the united atom state is not really approached, the effect may not be evident. Thus, in the nitrogen molecule considered above the two  $y\sigma$  electrons are anti-bonding, but the  $x\sigma$  orbitals are not; this is in agreement with the fact that the difference in energy between the  $2s$  and  $3p$  levels is greater than that between  $2p$  and  $3s$  levels. Apart from the four *KK* electrons, which are said to be "non-bonding," and the two anti-bonding electrons, the remaining eight have a "bonding"

Initial Atom.	Molecule.	United Atom.
$2s$	$z\sigma$	$2s$
	$y\sigma$	$3p$
$2p$	$x\sigma$	$3s$
	$w\pi$	$2p$
	$v\pi$	$3d$
	$u\sigma$	$4p$

effect. The large excess of bonding over anti-bonding electrons results in the nitrogen molecule being stable.

According to Herzberg (1929), to whom the idea of bonding and anti-bonding electrons is essentially due, the valency of an atom in a given compound is defined as half the difference in the number of bonding and anti-bonding electrons: this certainly leads to the conventional value of three for the valency of nitrogen, but the rule has been criticised as being artificial, since there can be various degrees of promotion, leading to increase of potential energy and anti-bonding, and varying amounts of energy decrease for non-promoted electrons, which aid bonding. According to the molecular-orbital theory there is no hard-and-fast distinction between bonding, anti-bonding and non-bonding electrons, and it is in fact a feature of the theory that a definite valency number cannot be attributed to an atom. It may be said that in the nitrogen molecule, for example, since the effect of the two non-bonding



cancels that of two bonding electrons, so that these four play no part, the remaining six electrons only are involved in bonding; the sharing of six electrons between two nitrogen atoms would be in harmony with the electronic theory based on classical ideas. Actually, the orbital theory postulates that all ten electrons are involved in the formation of the molecule: it is true that the anti-bonding action of the two  $y\sigma$  orbitals is partly neutralised by the bonding effect of the  $z\sigma$  orbitals, but this is not the same as saying that they play no part. Since, as already emphasised, each molecular orbital, according to the theory, represents the resultant of all the other electrons and the nuclei, it is evident that in the formation of a bond all the electrons must play some part.

**Unstable Molecules.** The anti-bonding influence accounts in the orbital theory for the facts that  $\text{He}_2$  and  $\text{Ne}_2$  molecules are not stable. In a helium atom, for example, the two orbitals are  $1s$ , but in the  $\text{He}_2$  united-atom two electrons would have to be promoted to  $2p$  orbitals; the increase of energy is so great that the anti-bonding effect of these electrons would outweigh the bonding effect of the other two orbitals. An analogous factor is responsible for the instability of the  $^3\Sigma$  state of the hydrogen molecule. In the stable  $^1\Sigma$  state the configuration must be  $(1s\sigma)^2$ , since the two electrons have anti-parallel spins (p. 65), but in the  $^3\Sigma$  state, wherein the spins are parallel, the Pauli principle requires one of the electrons to be in a different quantum level, and the configuration is probably  $(1s\sigma)(2p\sigma)$ , according to Mulliken's chart. The powerful anti-bonding effect of the promoted electron, from  $1s$  to  $2p$ , is quite sufficient to oppose any bonding influence exerted by the  $1s\sigma$  electron. The neon molecule  $\text{Ne}_2$  would have the configuration  $KK(z\sigma)^2(y\sigma)^2(x\sigma)^2(w\pi)^2(v\pi)^4(u\sigma)^2$ , but the two  $u\sigma$  orbitals are so strongly anti-bonding, as shown by the scheme on p. 82, that the molecule is very unstable.

**The Oxygen Molecule.** One of the most striking triumphs of the configuration theory as applied to the method of molecular orbitals is in connection with the structure of the oxygen molecule: it has long been a problem to account for the paramagnetism in such a way as to harmonise with the other properties of the  $\text{O}_2$



molecule. The oxygen atom in its ground state may be represented as  $1s^2 2s^2 2p^4$ , and in the combination of two atoms to form a molecule the configuration, resulting from the gradual filling up of the electron groups in order of decreasing strength of binding to the nuclei, becomes

$$KK(z\sigma)^2(y\sigma)^2(w\pi)^4(x\sigma)^2(v\pi)^2.$$

Since a  $\pi$  group can accommodate four electrons, it is clear that the  $v\pi$  shell is incomplete, and the arrangement of the two electrons present must be considered. If they adopt the same orbital then the Pauli principle requires that their spins should be opposed, and the resultant spin is zero; on the other hand, if the electrons are in different  $v\pi$  orbitals their spins may be either parallel or anti-parallel, so that the resultant spin can be unity or zero, respectively. For the first of the three possible cases the quantum number  $\lambda$  must have a value of  $\pm 1$  for each atom, so that the molecule is in a  $^1\Delta$  state (see p. 12); in the second and third cases the  $\lambda$  values are equal to unity, but opposite in sign, so that their sum is zero and both represent  $\Sigma$  states. The former, with the resultant spin of unity is, of course,  $^3\Sigma$ , and the latter with zero spin is  $^1\Sigma$ . It can be shown theoretically, and is found to be so spectroscopically, that the  $^3\Sigma$  state has the least potential energy, and so represents the stable form of molecular oxygen in its ground state. In this form the spins of the two  $v\pi$  electrons are not coupled to zero, and hence the molecule must be paramagnetic. The same arguments apply to the  $S_2$  molecules of sulphur, and there is reason to believe that the vapour of this substance is also paramagnetic. The explanation of the paramagnetism of oxygen proposed by Heitler and Pöschl (1934) involves a complex argument, concerning the coupling of different states, which is by no means easy to follow in comparison with that given above.

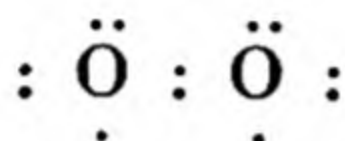
The conventional representation of the oxygen molecule in the ground state as given on p. 15 is of course unsatisfactory, as it does not indicate the existence of magnetic properties, and various alternatives have been proposed. Pauling (1931) has suggested a structure with one duplet and two triplet linkages,



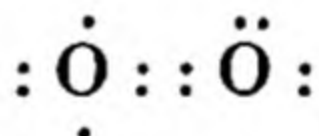
the possible existence of which can be justified as previously shown (p. 69), viz.,



This would account not only for the magnetic properties, since there are two uncoupled electrons in the molecule, but also for the heat of dissociation and the vibration frequency (see Chapter IV.), which are close to those for a normal double bond, as each electron triplet is supposed to have half the effect of an electron pair. Another possibility is the structure



with a single pair of electrons joining the two atoms (cf. Steiner, 1934), but this would not be in harmony with the energy of dissociation and the frequency of vibration as determined from the molecular spectrum of oxygen. Strictly speaking the molecular-orbital configuration cannot be represented in the usual manner, with dots to indicate the arrangement of electrons, but if a compromise were possible the oxygen molecule could be depicted as



indicating that a pair of electrons on the left-hand oxygen atom are not coupled to zero spin (Hunter and Samuel, 1934). Since the two oxygen atoms are probably not different, it may be assumed that there is a continual interchange of electrons between them, so that each has the odd pair of electrons for half the time. It is possible that this view is not fundamentally different from Pauling's suggestion of the three-electron bonds.

**Molecular Orbitals and the Valency Concept.** It is important to point out that the general basis of the molecular-orbital treatment implies a state of affairs fundamentally different from that involved in the concept of valency as generally accepted. Instead of regarding the molecule as made up of atoms, or ions, held together by valency bonds, the molecular-orbital point of view treats the molecule as a distinct entity built up of nuclei and electrons which happen to be supplied by the constituent atoms. It is not



possible to associate different molecular orbitals with different attached atoms, for in general all the atoms participate in the construction of a given orbital. For example, of the eight molecular orbitals directly involved in the structure of carbon dioxide, six are concerned with the carbon atom and *both* oxygen atoms; the conventional formulation of definite bonds joining one oxygen atom or the other to the carbon has here no significance. According to Mulliken (1931) the single bonding electron is the unit of valency, with the anti-bonding electron as a negative unit; the symmetrically related electron pair is regarded as a common *secondary* unit, although the actual pairing is thought to be merely incidental, as far as chemical binding is concerned, and to result only from the necessity of obeying the Pauli principle.

It may appear at first sight that the molecular-orbital concept permits of the possibility of two atoms being held together by a single electron, but consideration shows that this is so under certain limited conditions. It is only when there is approximate symmetry of the potential field with respect to the two-atoms concerned that a single electron can be regarded as having an appreciable bonding effect. In these circumstances there is no tendency for the electron to favour one particular atom of the two, and consequently, from wave-mechanical considerations, it follows that exchange energy must be included and it is this which leads to binding between the two atoms. The single bonding electron of the molecular-orbital theory is therefore identical with the one-electron bond of Pauling (p. 68). When the exchange effect is not operative a single electron has no bonding power. Mulliken is of the opinion that the odd-electron bonds, which may well occur in nitric oxide, nitrogen dioxide and in the  $O_2'$  ion (Neuman, 1934), consist of an even number of bonding electrons and one anti-bonding electron; for example, in nitric oxide there would be six bonding and one anti-bonding orbitals. This suggestion accounts in a simple manner for the fact that the "three-electron bond," postulated by Pauling, has only half the strength of a normal, that is two-electron, bond. In nitric oxide the bond strength would thus be equivalent to five shared electrons instead of seven as depicted on p. 69: this is



in much better agreement with the observed vibration frequency of the molecule, which is about  $1,900\text{ cm.}^{-1}$  (see p. 251). A combination of two bonding and one non-bonding electron would also account for the existence of the hydrides  $\text{CaH}$  and  $\text{MgH}$ , as indicated by band spectra: these substances involve a union of a hydrogen atom, with one electron, and a normal calcium or magnesium atom having paired electrons. Their energy of dissociation is about 30,000 cal. per gm. mol., and although less than that required for a normal bond is still quite considerable. The appreciable stability of the radicals is not easily explained by the electron-pair bond theory, especially as the inclusion of exchange energy does not seem probable in these cases.

**Conclusion.** Although the molecular-orbital method has opened up new possibilities in connection with the subject of valency, it is doubtful whether it is yet sufficiently developed to displace the classical views of localised valency bonds and of the electron-pair as the fundamental unit corresponding to a single linkage, both of which obtain support from the Heitler-London method of treatment. These views will, therefore, continue to be adopted by chemists who have found them so fruitful in many ways, although it should be noted that neither of the procedures based on wave mechanics limits the electron shell to the octet, except in the first period of the periodic classification. It must be emphasised in spite of the fact that the molecular-orbital viewpoint does not require directional bonds, it still postulates, as indicated above, definite arrangements of the nuclei so as to give the most stable structures; the concepts of stereochemistry, in their widest sense, therefore, remain unaffected and possibly strengthened.

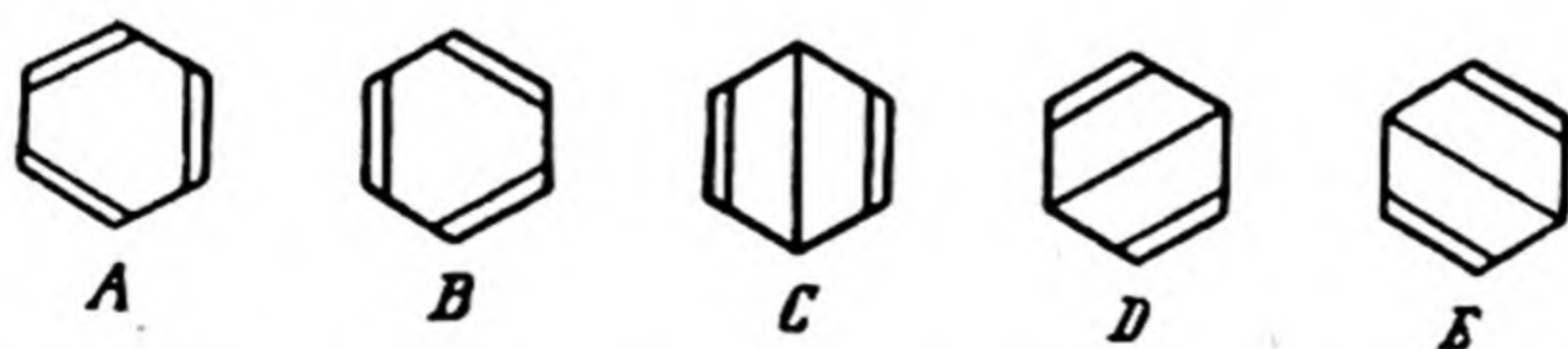
## RESONANCE

One of the most interesting consequences of the application of quantum mechanics to chemistry is in connection with the phenomenon which, following Pauling (1933), has become widely known under the name of "resonance." If the *electronic* structure of a molecule can be depicted in two or more ways in which the positions of the atoms remain unchanged, and the energies of



the various states do not differ considerably from one another, then the wave function of the actual molecule can be written down, at least approximately, as a linear combination of the orbital functions of the separate structures. The potential energy of the system can then be calculated and it is found that one solution of the appropriate equations gives a value which is less than that for any of the individual structures. The possibility of the existence of several electronic arrangements of similar energy consequently results in increased stability. This effect is known as "resonance," and the molecule is said to "resonate between" the various possible states. At one time it was considered that the molecule actually spent part of its time in all the possible states, the change from one to another occurring at very high frequency, so that the term resonance had some sort of physical meaning, but this view has been generally discarded. The interpretation now given to resonance is that as a result of the possibility of several electronic structures for a molecule, the real state is a combination of these which is actually more stable. The difference between the potential energy in this "stationary state" and that of the states which contribute in a linear manner to the wave function of the molecule is called the resonance energy; it is this, which of course has a negative value, that is responsible for the stabilisation.\*

**Resonance in the Benzene Molecule.** An instructive example of the effect of resonance is exhibited by the benzene molecule (Hückel, 1931, 1932; Pauling and Wheland, 1933): if the six carbon atoms, with their attached hydrogen atoms, may be regarded as occupying the corners of a hexagon, then five independent structures, the so-called "canonical set of structures," are possible, as shown below.



\* Resonance energy is another aspect of the "exchange energy," which is a direct consequence of quantum-mechanical treatment, that has been already mentioned in various connections.



All other electronic arrangements can be represented by combination of those depicted. Of these  $A$  and  $B$  are Kekulé structures, and  $C$ ,  $D$  and  $E$  are Dewar formulæ; the Claus formula can be represented as a linear combination of these five canonical structures, thus  $C + D + E - A - B$ . It may be observed that the formulæ  $C$ ,  $D$  and  $E$  imply the presence of a *para*-bond: this is probably not the case, the bond being actually ineffective and may perhaps be represented more accurately by an ionic structure in which the two electrons remain associated with one of the carbon atoms. States such as these are generally called "excited structures."

The benzene molecule is regarded as involving essentially six electrons only, one on each carbon atom, since the remainder are used to form ordinary single bonds between carbon and carbon, and carbon and hydrogen. By means of the relationship of equation (x.), using the method of electron pairs, it can then be shown that for a single Kekulé structure the resonance energy is  $1.5J$ , where  $J$  is the exchange integral between the electrons associated with two adjacent atoms. The exchange integrals for electrons on non-adjacent atoms have been ignored in the calculation. For resonance between the two Kekulé structures  $A$  and  $B$ , the exchange energy is  $2.4J$ , whereas for all five canonical structures it is found to be  $2.606J$ ; the total resonance energy responsible for stabilisation is thus  $2.606J - 1.5J = 1.106J$ . The two Kekulé forms clearly provide the main contribution to the actual structure of benzene, although the excited structures are not without influence. It is resonance between the five forms, presumably leading to one which is in a sense a combination of them all, that gives to benzene and its derivatives their particular chemical properties. The value of the exchange integral  $J$  cannot yet be calculated with any certainty, but it may be estimated by comparing the known heat of formation of benzene from its elements with the value obtained by assuming the additivity of the heats of the various linkages in a Kekulé structure, viz., three C—C, three C=C and six C—H bonds. The observed value is nearly 40,000 cal. per gm. mol. greater than that calculated, and if this is taken as equal to the stabilising resonance energy,



$1.106J$ , then  $J$  is found to be about 35,000 cal. Although this procedure is approximate, especially in so far as there is considerable uncertainty as to the exact additivity of heats of linkage, it is a striking fact that values of  $J$  of the same order are obtained by applying analogous methods to naphthalene, stilbene, triphenylbenzene and other aromatic hydrocarbons (Wheland, 1934). It is of interest to note that for naphthalene there are 42 canonical structures; of these the three unexcited forms contribute  $1.37J$ , the sixteen singly excited structures provide  $0.63J$ , and the remaining twenty-three doubly excited structures only  $0.04J$  (Sherman, 1934).

**Molecular-Orbital Treatment.** The method of molecular orbitals has also been applied to calculate the potential energy of benzene, which is also treated as a system of six electrons, one associated with each carbon atom. The resonance energy calculated in this manner is somewhat different from that given by the method of localised pairs, but it is a striking fact that the ratio of the  $J$  values obtained by the two methods is almost constant at 1.8 for a number of hydrocarbons. One exception is provided by the four-membered ring *cyclobutadiene*: the localised-pair method indicates that there is a resonance energy equal to  $J$ , whereas the molecular-orbital procedure leads to the conclusion that there is no stabilising effect due to resonance.

**Internuclear Distances.** Further interesting light on the subject of resonance is thrown by a consideration of the internuclear distances in benzene: X-ray examination of the crystals and electron-diffraction study of the vapour (see "Recent Advances in General Chemistry," Chapter V.) have shown that the carbon-carbon distance has a *constant* value of about  $1.40\text{\AA}$ . The normal single-bond distance between two carbon atoms is  $1.54\text{\AA}$ ., and the double-bond distance is  $1.38\text{\AA}$ ., so that *all* the bond lengths tend to approach the double-bond value. The fact that all the distances are the same is just what is to be expected from the point of view of resonance, and the approach to the shorter bond length indicates, as found in many cases, that the inter-atomic distances in the actual "stationary state" of the molecule tend to approach those for multiple rather than single bonds.

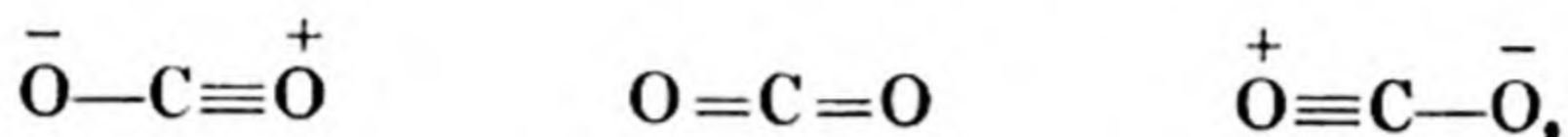


**Detection of Resonance.** The two most important methods for detecting the existence of resonance are those described, namely measurement of the heat of formation and of the internuclear distances in the compound. Of these the former is less reliable, and may in fact sometimes be misleading, since it is based on the assumption of the additivity of the heats of formation of linkages which may not be altogether justified. Pauling and Sherman (1933) compared the experimental heats of formation of a number of organic compounds with the calculated values assuming additivity, and found differences of the order of 20,000 to 30,000 cal. per gm. mol., attributed to resonance, for a number of monobasic and dibasic carboxylic acids, aliphatic amides and urea. In all these instances there is no difficulty in formulating alternative electronic structures with the positions of the atomic nuclei virtually unchanged.

**Carbon Monoxide.** The measured heat of formation of carbon monoxide is about 240,000 cal. per gm. mol., although the heat of formation of the C=O linkage in ketones is only 178,000 cal. This result suggests that resonance is occurring between the normal structure C=O and the alternative formulation  $\overset{-}{\text{C}}\equiv\overset{+}{\text{O}}$ . The conclusion that carbon monoxide has the latter structure has been questioned by Hunter and Samuel (1934), who suggest that it is not justifiable to compare carbon monoxide with the carbonyl group of a ketone. There is, however, other evidence for the  $\overset{-}{\text{C}}\equiv\overset{+}{\text{O}}$  structure (see pp. 115, 177), but the best argument for resonance appears to be that based on the internuclear distance. The normal separation of doubly-bound carbon and oxygen should be 1.28Å (see "Recent Advances in General Chemistry," Chapter V.), but the actual distance between the nuclei has been found to be 1.15Å., which is so close to the triple-bond distance as to favour the suggestion that resonance occurs in carbon monoxide between the two structures mentioned above. It may be noted that a third configuration  $\overset{+}{\text{C}}-\overset{-}{\text{O}}$  is also possible, but its wave function probably contributes little to the actual state of the molecule.

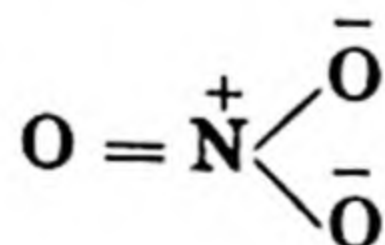


**Carbon Dioxide.** There is good evidence that in carbon dioxide also there is resonance between at least three possible structures, viz.,



the middle one being the formula generally accepted. The measured heat of formation is about 380,000 cal., whereas the value calculated on the assumption of additivity is approximately 348,000 cal. for all three forms depicted; there are four bonds from carbon to oxygen in each case, and the heat of formation, or dissociation, of any linkage is approximately proportional to the number of bonds involved (see p. 254). The greater stability of the actual molecule, by 32,000 cal. per gm. mol., suggests that resonance occurs between the three structures. If this is the case, then from what has been already said in connection with benzene, both carbon-oxygen distances should be the same, but should approach the triple-bond distance of 1.14Å.; the actual value is 1.15Å. in each case, a result in excellent agreement with the resonance concept.

**Nitrate and Carbonate Ions.** Mention has been already made of the difficulty concerning the apparently unsymmetrical structure of the nitro-group (p. 84), a difficulty enhanced by the fact that its dipole moment (Chapter III.) acts in such a way as to indicate a symmetrical arrangement. The obvious explanation is that resonance is occurring between the two identical structures depicted on p. 169. Confirmation for this view could be obtained from measurement of the N—O distances, but the only results available (James, King and Horrocks, 1935) are too unexpected to be accepted with confidence. The nitrate ion, however, presents an essentially similar problem. The conventional structure



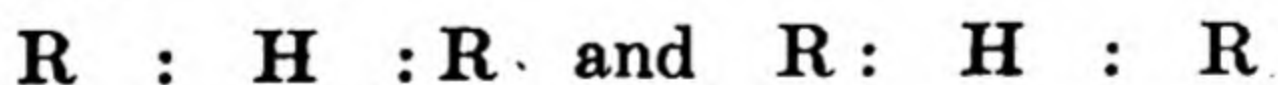
is obviously not in harmony with the fact that crystallographic evidence shows the three N—O distances to be the same, and since there is a possibility of three structures which are identical,



except for the fact that the apparently double-bonded oxygen is different in each case, resonance is clearly indicated. The three nitrogen-oxygen distances in the nitrate ion are equal, having a value of  $1.28\text{\AA}$ ., in excellent agreement with the value expected for  $\text{N}=\text{O}$ , namely  $1.22\text{\AA}$ .. The question of the structure of the carbonate ion is analogous: again, resonance between three electronic formulations is possible, and each carbon-oxygen distance should approach the  $\text{C}=\text{O}$  value, namely  $1.28\text{\AA}$ .. The observed distances are all  $1.23\text{\AA}$ ., which are even smaller than expected, but it is not known if this has any significance, or if it is due to experimental error. There are many other cases in which resonance has been indicated by the measurement of inter-nuclear distances, and several of these are discussed in the companion volume to this work, "Recent Advances in General Chemistry."

### CO-ORDINATED HYDROGEN

Although the phenomenon of co-ordinated hydrogen is established beyond doubt (p. 47), there has been some difficulty concerning its electronic formulation, since a group of four electrons around a hydrogen atom, which the bi-covalency would imply, is forbidden by the Pauli principle. The concept of resonance, which has been applied in this connection by Sidgwick (1933, 1934), has helped very considerably to clarify the situation. In a system  $\text{R}\cdot\text{H}\cdot\text{R}$ , for example, there can be resonance between the two structures

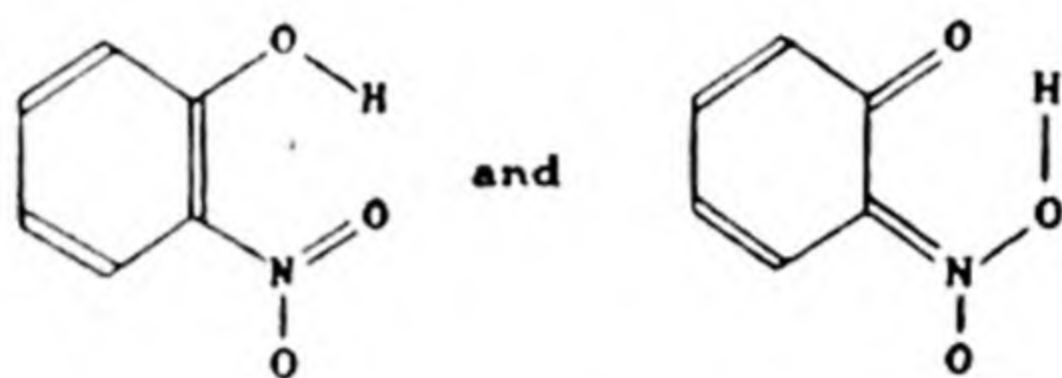


in which the atomic nuclei are not moved, and the only difference is due to the change in position of the two pairs of electrons shown. The two structures clearly have identical energies, and so resonance should occur, with consequent stabilisation of a state which is something combining the two, although it cannot be depicted in a conventional manner. Whenever there is this possibility of a hydrogen atom changing its allegiance as a result of electron movement, so that two states of similar energy are possible, co-ordination occurs because of the phenomenon of resonance.

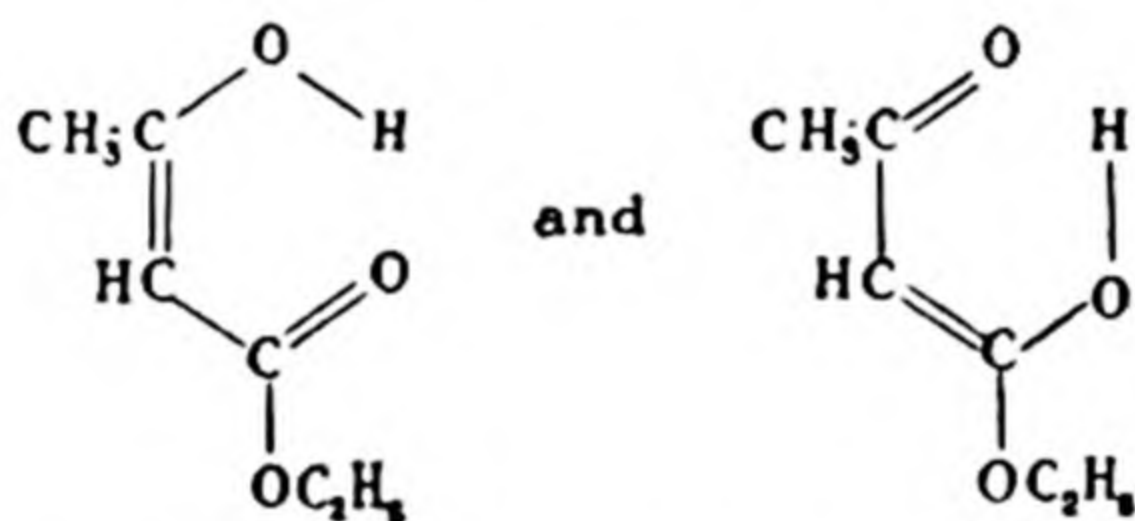
In discussing examples of this type of behaviour, Sidgwick (1934)



considers two possibilities. The first occurs when the hydrogen atom can be linked without ionisation to either of the two atoms it holds together; the two atoms are then part of the same molecule, and a rearrangement of links takes place along the chain which is joined up through the hydrogen atom to form a ring. Illustrations of co-ordination of this kind are shown on pp. 51 and 52; for *o*-nitrophenol, for example, resonance occurs between the structures



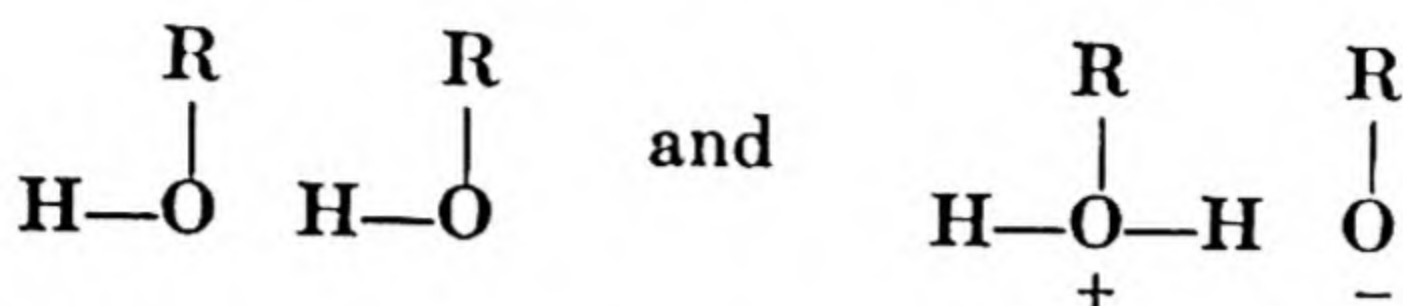
and for acetoacetic ester the resonating structures are



In both examples the configurations of the atomic nuclei remain unchanged, although the electrons are distributed differently. The resonance between the two structures serves to keep the two oxygen atoms bound together in the form of a ring. It is of special interest to record that when a  $\beta$ -keto-ester is reduced to the corresponding  $\beta$ -keto-alcohol, the tendency to form a ring through co-ordinated hydrogen practically disappears; there is now no possibility of the movement of the  $C=O$  bond from one oxygen to the other.

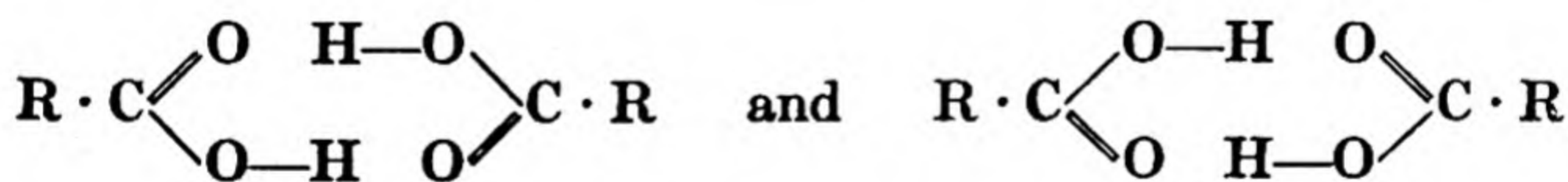
The second type of resonating structure connected with co-ordinated hydrogen occurs generally with simple hydroxylic compounds, and is responsible for the association of such substances as water, alcohol and phenols, and possibly for the existence of certain molecular compounds. With two molecules of alcohol, for example, there are two possible arrangements,





so that resonance can occur: the two molecules are held together, and the associated system stabilised, by the resonance energy. By introducing further molecules of alcohol in a chain it can be easily shown that in the excited state, that is the ionised form, the two ions are separated by a chain of normal molecules, so that almost unlimited association is possible. It must not be imagined that, because an ionic structure is suggested as a possible state, it is implied that free ions are present to any great extent: because of resonance the ions are not free, and in the actual molecule, which is a combination of the possible resonating structures, there may be no ionisation at all.

Carboxylic acids form a class which may be regarded as being intermediate between those already considered; with these substances association is not altogether of the indefinite type which apparently occurs with water and alcohols, but leads generally to the formation of definite double molecules in solid, liquid and vapour states. The resonating structures are probably to be depicted thus



and they are, of course, identical. The result is virtually equivalent to ring formation, and as a result there is a movement of the double bonds but no ionisation.

As stated previously, it does not appear possible to depict exactly what is the real structure of a substance stabilised by resonance involving co-ordinated hydrogen, and so for the present it is convenient to retain the formulation used in earlier parts of this chapter, generally involving an arrow. It is important, however, to remember the limitations of this method of representation. Before the concept of resonance was developed Sugden (see p. 52) had suggested that in compounds with co-ordinated hydrogen the two atoms held together by the hydrogen



were bound to the latter by single-electron linkages. The resonance view implies that the hydrogen never has more than two electrons associated with it, and these are shared with either one atom or the other; on the average it may be supposed, therefore, that it shares a single electron with each of the atoms which it bridges. In a sense, therefore, the singlet linkage suggestion may be regarded as correct, although it must be pointed out that singlet linkages alone are not sufficient to account for the stability of rings containing co-ordinated hydrogen: it is the resonance energy which is the real factor responsible.

### REFERENCES

- BENNETT and PHILLIP. *J. Chem. Soc.*, 1928, 1930, 1937.  
 BENNETT and WILLIS. *Ibid.*, 1929, 256.  
 BILTZ and KLEMM. *Z. anorg. Chem.*, 1926, 152, 267.  
 BOHR. *Phil. Mag.*, 1913, 26, 1, 476, 587; "The Theory of Spectra and Atomic Constitution," 1922\*.  
 BURY. *J. Amer. Chem. Soc.*, 1921, 43, 1602.  
 CLARK. *Chem. Reviews*, 1932, 11, 281\*.  
 DUSHMAN. *J. Chem. Ed.*, 1931, 8, 1074\*.  
 FAJANS. *Z. Physik*, 1924, 23, 1; *Z. Elektrochem.*, 1928, 34, 502\*.  
 GRIMM. *Z. Elektrochem.*, 1928, 34, 430\*.  
 HEITLER. *Physikal. Z.*, 1930, 31, 185; *Z. Physik*, 1931, 68, 12.  
 HEITLER and LONDON. *Ibid.*, 1927, 44, 455; 1928, 46, 455.  
 HINSHELWOOD. *Ann. Reports*, 1932, 29, 17\*; 1933, 30, 44\*.  
 HÜCKEL. *Z. Physik.*, 1930, 60, 423.  
 HUND. *Z. Elektrochem.*, 1928, 34, 437; *Z. Physik*, 1931, 73, 1.  
 HUNTER and SAMUEL. *J. Chem. Soc.*, 1934, 1180; *Chem. and Ind.*, 1935, 467.  
 JAMES and COOLIDGE. *J. Chem. Physics*, 1933, 1, 825.  
 JEVONS. "Report on Band Spectra," 1932\*.  
 KOSSEL. *Ann. Physik*, 1916, 49, 229.  
 LATIMER and RODEBUSH. *J. Amer. Chem. Soc.*, 1920, 42, 1431.  
 LENNARD-JONES. *Trans. Faraday Soc.*, 1929, 25, 668.  
 LEWIS. *J. Amer. Chem. Soc.*, 1916, 38, 762; *J. Chem. Physics*, 1933, 1, 17\*; "Valence and the Structure of Molecules," 1923\*.  
 LONDON. *Z. physikal. Chem.*, 1930, B11, 222.  
 LOWRY. *Chem. and Ind.*, 1923, 42, 43, 316, 412, 711; 1924, 43, 218; *J. Chem. Soc.*, 1923, 123, 822; *Trans. Faraday Soc.*, 1923, 19, 285; 1928, 24, 1.  
 LOWRY and BURGESS. *J. Chem. Soc.*, 1923, 123, 2111.  
 MENZIES. *Ibid.*, 1934, 1755.  
 MOORE and WINMILL. *Ibid.*, 1912, 101, 1675.  
 MULLIKEN. *J. Chem. Physics*, 1933, 1, 492; 1934, 2, 400; 1935, 3, 375, 506, 564, 573, 586, 635, 720; *Rev. Mod. Physics*, 1932, 4, 1\*.  
 NEUMAN. *J. Chem. Physics*, 1934, 2, 31.  
 PANETH. *Ber.*, 1920, 53, 1710.  
 PAULING. *Chem. Reviews*, 1928, 5, 185\*; *J. Amer. Chem. Soc.*, 1931, 53, 1367, 3225; 1932, 54, 988, 3570; *J. Chem. Physics*, 1933, 1, 362, 606, 679.  
 PENNEY. *Proc. Roy. Soc.*, 1934, 144A, 166; 146A, 223; *Trans. Faraday Soc.*, 1935, 31, 734; "The Quantum Theory of Valency," 1935\*.



- PENNEY and SUTHERLAND. *J. Chem. Physics*, 1933, 1, 492.
- RODEBUSH. *Chem. Reviews*, 1928, 5, 509\*.
- SIDGWICK *et al.* *J. Chem. Soc.*, 1923, 123, 725 ; 1924, 125, 527, 2672 ; 1925, 127, 909, 2739 ; 1930, 2027 ; 1936, 533\* ; *Chem. and Ind.*, 1923, 42, 1203 ; *Trans. Faraday Soc.*, 1923, 19, 469 ; *Z. Elektrochem.*, 1928, 34, 430 ; *Chem. Reviews*, 1931, 9, 77\* ; "The Electronic Theory of Valency," 1927\* ; "The Covalent Link in Chemistry," 1932\* ; *Ann. Reports*, 1933, 30, 110\* ; 1934, 31, 37\*.
- SIDGWICK and BAILEY. *Proc. Roy. Soc.*, 1934, 144A, 521.
- SLATER. *Phys. Rev.*, 1931, 37, 481 ; 38, 1109.
- SUGDEN. *J. Chem. Soc.*, 1932, 161, 246 ; 1935, 621.
- MAIN SMITH. *Chem. and Ind.*, 1923, 42, 1073 ; 1924, 43, 323 ; *Phil. Mag.* 1925, 50, 878.
- STONER. *Ibid.*, 1924, 48, 719.
- THOMPSON. *Ann. Reports*, 1933, 30, 56\*.
- THOMSON. *Phil. Mag.*, 1904, 7, 237.
- UREY. *J. Chem. Ed.*, 1931, 8, 1114\*.
- VAN VLECK. *Chem. Reviews*, 1928, 5, 467\* ; *J. Chem. Physics*, 1933, 1, 177, 219 ; 1934, 2, 20, 297, 357.
- VAN VLECK and SHERMAN. *Rev. Mod. Physics*, 1935, 7, 167\*.
- WHELAND. *J. Chem. Physics*, 1934, 2, 474.
- WILSON. *J. Amer. Chem. Soc.*, 1934, 56, 746.

\* Review papers and books, wherein further references are to be found, are marked by an asterisk.



## CHAPTER II

## THE PARACHOR

SINCE the middle of the past century many attempts have been made to discover physical properties of compounds which are additive functions of their chemical compositions ; one of the most successful of these, known as the "parachor," has been suggested recently by Sugden (1924). It has already proved very helpful in solving problems connected with the structure of various compounds and radicals.

## MACLEOD'S EQUATION

In 1928 Macleod discovered an empirical relationship between the surface tension of a liquid ( $\gamma$ ) and its density ( $D$ ), thus

$$\gamma = C' (D - d)^4 \quad . \quad . \quad . \quad . \quad . \quad . \quad (\text{i.})$$

or

$$C = \frac{\gamma^{\frac{1}{2}}}{D - d} \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \quad (\text{ii.})$$

where  $d$  is the density of the vapour at the same temperature as used in the measurement of  $\gamma$  and  $D$ ;  $C$  is a constant for each particular substance and, for non-associated liquids, is independent of temperature over a very considerable range. The applicability of Macleod's equation is well demonstrated by the results given in Table XII. (Sugden, 1924) on p. 99.

These figures, which are typical of those obtained for many compounds, indicate that the suggested relationship between surface tension and density holds up to within a few degrees of the critical temperature; even the divergence here, *e.g.*, benzene at  $280^{\circ}$ , may be due to experimental error owing to difficulties of measurement. For associated substances, *e.g.*, alcohols, the value of  $C$  is not so constant, but increases as the temperature is raised.



TABLE XII.—*Test of Macleod's Equation*

Benzene.		Diethyl Ether.		Carbon Tetrachloride.	
Temp.	C.	Temp.	C.	Temp.	C.
20°	2.638	20°	2.857	20°	1.429
41.5°	2.642	50°	2.865	33°	1.429
61°	2.647	80°	2.850	46°	1.432
90°	2.646	110°	2.865	90°	1.433
120°	2.643	140°	2.865	120°	1.431
150°	2.650	170°	2.884	150°	1.425
180°	2.641	185°	2.947	180°	1.429
240°	2.657			210°	1.444
270°	2.739			240°	1.419
280°	3.372			270°	1.405
Crit. Temp. 288.5°		193°		283°	

### THE PARACHOR

If both sides of the second form of Macleod's equation (ii.) are multiplied by the molecular weight of the compound, then

$$MC = \frac{M\gamma^{\frac{1}{2}}}{D - d} = \text{a constant, } [P], \quad . . . . . \text{(iii.)}$$

since both  $M$  and  $C$  are constants for the given substance. The resulting constant  $[P]$  is called the "parachor" of the compound, and in view of the constancy of the quantity  $C$ , as shown in Table XII., the value of the parachor is also remarkably independent of temperature over a wide range. At most temperatures the density  $d$  of the vapour is negligibly small, and may be neglected in comparison with  $D$ , and so the term  $M/(D - d)$  may be replaced by  $M/D$ , which is equal to the molecular volume ( $V$ ) of the liquid; hence

$$[P] = V\gamma^{\frac{1}{2}} \quad . . . . . \text{(iv.)}$$

If the temperature is imagined to be such that the surface tension is unity, then the parachor would be equal to the molecular volume or, in other words, the parachor may be regarded as the molecular volume of a compound when its surface tension is unity.



A comparison of the parachors of different substances is thus equivalent to the comparison of molecular volumes at temperatures at which the liquids have the same surface tension.

**The Parachor as a Molecular Volume.** The fact that the parachor is really equivalent to a molecular volume may be shown in two ways. In the first place the ratio of the parachor to the molecular critical volume ( $V_c$ ) of a given compound has an almost constant value of 0.77 for all substances; some values for  $[P]$  and  $V_c$ , and their ratio, are given in Table XIII. (Sugden, 1924).

TABLE XIII.—*Comparison of Parachors and Molecular Critical Volumes*

Substance.	$[P]$ .	$V_c$ .	$[P]/V_c$ .
Propyl acetate . . . .	256.1	345.3	0.74
Ethyl propionate . . . .	254.8	344.3	0.74
Hydrogen . . . . .	35.1	46.9	0.75
Diethyl ether . . . . .	211.7	281.9	0.75
Carbon tetrachloride . . . .	219.9	276.1	0.80
Benzene . . . . .	206.3	256.1	0.81

Secondly, if  $[P]$  represents a molecular volume then  $[P]^{\frac{1}{3}}$  should be approximately proportional to the cross-sectional area of the molecule. Sugden has compared the values of  $[P]^{\frac{1}{3}}$  with the cross-sectional, or "collision," area of molecules determined from viscosity measurements, and has found a very satisfactory constant ratio.

**Additivity of the Parachor.** It is well known that the molecular volumes of liquids determined by Kopp (1842) at the boiling point were, approximately at least, an additive function of the chemical composition, and hence it was reasonable to suppose that the same additivity would apply to the parachor; this has proved to be definitely the case. The first indication of this additivity was shown by Sugden's observation that isomeric substances of similar constitution have the same parachor; this is illustrated by the results in Table XIV.



TABLE XIV.—*Parachors of Isomeric Compounds*  
Esters of Formula  $C_6H_{12}O_2$ .

Substance.	[P].	Substance.	[P].
<i>i</i> -Amyl formate. . .	293.6	Ethyl butyrate . . .	293.6
<i>i</i> -Butyl acetate . . .	295.1	Ethyl <i>i</i> -butyrate . . .	292.9
<i>n</i> -Propyl propionate . . .	295.3	Methyl valerate . . .	292.5

## Disubstituted Benzene Derivatives.

Substance.	Parachor.		
	Ortho.	Meta.	Para.
Xylene . . . . .	283.3	283.8	283.8
Nitrotoluene . . . . .	301.1	300.6	302.8
Chloronitrotoluene . . . . .	299.1	299.9	300.0
Toluenitrile . . . . .	290.6	295.6	294.4

Further, the difference in parachor between successive members of a homologous series should be constant and independent of the type of compound; this has been found to be the case, as the parachor values in Table XV. indicate.

TABLE XV.—*Parachors in Homologous Series*

Hydrocarbons.			Esters.			Ketones.		
Formula.	[P]	$\Delta$	Formula.	[P]	$\Delta$	Formula.	[P]	$\Delta$
$C_2H_6$	110.5		$C_2H_4O_2$	138.1		$C_3H_6O$	161.5	
		40.3			39.2			36.7
$C_3H_8$	150.8		$C_3H_6O_2$	177.3		$C_4H_8O$	198.2	
		$39.8 \times 3$			88.8			37.5
$C_4H_{10}$	270.1		$C_4H_8O_2$	216.1		$C_5H_{10}O$	235.7	
		39.2			$38.8 \times 2$			$39.2 \times 2$
$C_5H_{12}$	309.3		$C_5H_{10}O_2$	293.8		$C_6H_{12}O$	314.1	
		35.7			38.5			41.6
$C_6H_{14}$	345.0		$C_6H_{12}O_2$	332.3				
		$39.1 \times 2$			$38.6 \times 2$			
$C_{10}H_{22}$	424.2		$C_9H_{18}O_2$	409.6				

The average difference, which corresponds to the parachor of the  $CH_2$  group, has been found from the examination of several series to be 39.0.



**Atomic Parachors.** By subtracting from the parachor for a paraffin (formula  $C_nH_{2n+2}$ ) that for  $nCH_2$  groups, *i.e.*,  $39n$ , the parachor equivalent of two atoms of hydrogen can be found; the average difference for the series in which  $n$  varied from 2 to 10 was found to be 34.3, and so the atomic parachor of hydrogen was taken as 17.1. It is interesting to note that the parachor for liquid hydrogen ( $H_2$ ) is 35.1, which is in excellent agreement with the value calculated from measurements on organic compounds. Since the parachor for  $CH_2$  is 39.0, it follows that the value for the carbon atom must be 4.8. Proceeding in this manner it is possible, from the known parachors of C and H, to determine the values for other atoms; for example, that for oxygen is obtainable from measurements on ethers, for nitrogen from a study of amines, for halogens from an examination of halogenated hydrocarbons, and so on. Some of the values obtained by Sugden in this way, with slight alterations by Pearson and Robinson (1984), are quoted in Table XVI. (See also footnote, p. 105.)

TABLE XVI.—*Atomic Parachors*

Element.	Parachor.	Element.	Parachor.
Carbon . . .	4.8	Sulphur . . .	48.2
Hydrogen . . .	17.1	Fluorine . . .	25.0
Nitrogen . . .	12.5	Chlorine . . .	54.3
Phosphorus . . .	39.2	Bromine . . .	68.0
Oxygen . . .	20.0	Iodine . . .	90.0

It has been found that for certain long chain fatty acids the parachor equivalent for  $CH_2$  is more nearly 40.0 than 39.0, as suggested above (Mumford and Phillips, 1929); on the basis of this, and other results, a new distribution of atomic parachors has been proposed in which the values for carbon and hydrogen are 9.2 and 15.4 respectively. It should be noted, however, that for hydrogen, at least, the figure in Table XVI. appears preferable: in the first place it is in better agreement with the parachor of liquid hydrogen, and in the second place the value of



17 fits in with the tabulation made by Pearson and Robinson (1934) of the parachors of a number of hydrides.

**Structural Parachors.** As with other additive properties, so with the parachor, constitutional factors must be taken into account; for example, the parachor of ethylene ( $C_2H_4$ ) is found by experiment to be 99.5, whereas the value for two atoms of carbon and four atoms of hydrogen is 78. The same difference is observed for all substances containing a double bond, and a mean parachor contribution of 23.2 is attributed to the presence of such a linkage. A triple bond apparently adds 46.6 towards the parachor of the compound in which it occurs, and definite structural parachors must be included where there is ring formation. A structural factor of a somewhat different type has been found in esters; the mean parachor for a series of esters of general formula  $C_6H_{12}O_2$  (see Table XIV.) is 293.8, whereas the sum of the parachors for 6C and 12H is 233.0, and so the parachor for  $O_2$  in these esters is 60.8, instead of the normal value of  $40.0 + 23.2 = 63.2$  (two oxygen atoms and a double bond). A similar value has been found in all the esters examined. The structural parachor equivalents, as determined by Sugden and others, are given in Table XVII. A pyridine ring has the same effect on the parachor as a benzene ring (Ray, 1934), and a ring containing more than eight members behaves as a straight-chain compound (Ruzicka, 1933).

TABLE XVII.—*Structural Parachors*

Triple bond	.	.	46.6	4-membered ring	.	11.6
Double bond	.	.	23.2	5-membered ring	.	8.5
				6-membered ring	.	6.1
$O_2$ in esters	.	.	60.0	7-membered ring	.	4.6
				8-membered ring	.	2.4
3-membered ring	.	.	16.7	Naphthalene ring	.	12.2

It will be observed that no parachor has been attributed to a single linkage; this is not necessarily correct, but the atomic parachors determined from measurements on compounds, *i.e.*, the values given in Table XVI., really include the contribution of



such a linkage. In other words, the single bond is taken as an arbitrary zero level from which the effect of other structures is reckoned; generally these effects are positive, although it will be shown in the next section that they may be negative. There is some evidence, however, that the effect on the parachor of sharing an electron pair, which is the basis of a single linkage, is negligible. The parachor of liquid mercury has been determined as 69.4 per atom, whereas from measurements of the surface tension and density of mercury diphenyl,  $\text{Hg}(\text{C}_6\text{H}_5)_2$ , the parachor contribution of the mercury atom is found to be 68.7. In liquid mercury it is very probable that the molecules are monatomic, so that no electrons are shared, but in the diphenyl compound two single linkages are involved, for the mercury atom shares two pairs of electrons with the phenyl groups; the atomic parachors are, however, almost identical, and so it appears that a single bond has no parachor equivalent.

Although it has been assumed that atomic parachors generally remain constant irrespective of the nature of the compound in which the atoms are present, this is probably not strictly true. The parachor of hydrogen, which may be taken as 17.0–17.1 in carbon compounds, varies from 16 to 19 for most other substances, but is apparently as low as 10.3 in hydrogen fluoride, increasing to 14.7 in hydrogen iodide. It may be mentioned in this connection that Hunter and Samuel (1935) have proposed to attribute parachors to elements according to their state of combination, instead of adopting a definite value for each atom and allowing for various types of linkage. This procedure, of course, gives very satisfactory additivity, but has the disadvantage of being less fundamental than that already described.

**Semi-polar Linkage and the Parachor.** Reference has already been made (Chapter I.) to the desirability of distinguishing between two types of covalency, and it is of interest to note that this difference is reflected in a parachor effect. In the compounds phosphorus oxychloride, phenyl phosphate, sulphuryl chloride and methyl sulphate for example, it is probable that semi-polar bonds are present, and it is instructive to compare the parachors determined experimentally with the respective sums



of the atomic parachors ( $\Sigma[P]$ ). The results are given in Table XVIII.

TABLE XVIII.—*Parachors of Substances with Semi-polar Bonds*

Substance.	Formula.	[P] observed.	$\Sigma[P]$	$\Delta$
Phosphorus oxy-chloride .	$\text{Cl}_3\overset{+}{\text{P}}-\bar{\text{O}}$	217.6	220.6	— 3.0
Phenyl phosphate .	$(\text{C}_6\text{H}_5\text{O})_3\overset{+}{\text{P}}-\bar{\text{O}}$	686.5	687.7	— 1.2
Sulphuryl chloride .	$\text{Cl}_2\overset{++}{\text{S}}\begin{matrix} \diagup \bar{\text{O}} \\ \diagdown \bar{\text{O}} \end{matrix}$	193.3	196.8	—1.75 $\times$ 2
Methyl sulphate .	$(\text{CH}_3\text{O})_2\overset{++}{\text{S}}\begin{matrix} \diagup \bar{\text{O}} \\ \diagdown \bar{\text{O}} \end{matrix}$	238.9	240.4	—0.75 $\times$ 2

The difference between the observed and calculated results has been found for many other compounds in which there is reason to believe that a semi-polar link is present; this difference is so persistent, and so much larger than the normal divergences from the parachor, that it must have a definite significance. From an examination of a number of substances it has been concluded that on the average the presence of a semi-polar bond *reduces* the parachor by 1.6 units.\*

**Parachor Anomalies.** It is apparent that Sugden's method of distributing parachor equivalents amongst various elements and bonds is not the only possibility; Sippel (1930) has indicated a number of suggestions, and an alternative system has been worked out completely by Mumford and Phillips (1929). An essential feature of this scheme is the inclusion of allowances, known as strain constants, for branching chains, for negative groups, *e.g.*, Cl, CN, COOR, OR, and for alkyl substituents in the benzene nucleus. Although this method of treating parachors is of interest, its application appears to be much more complicated

\* Mann and Purdie (1935) state that Sugden now attributes no parachor equivalent to the co-ordinate link; this is based on the following revised atomic parachors: C, 7.2; H, 16.2; O, 20.0; Cl, 53.5; Br, 68.0; S, 48.5.



than the Sugden system, and so the latter, as given above, is generally employed. It must be admitted, however, that it is by no means complete, and will no doubt have to be modified. In addition to the variation of the parachor of hydrogen, according to the nature of the atom with which it is linked, mention may be made of the fact that the contribution of two  $\text{CH}_2$  groups varies from 70.8 to 78.4, when the parachors of a series of esters of substituted glutaric acids are compared with the corresponding compounds of malonic acid (Vogel, 1934). The accumulation of negative groups also has an influence on the parachor, as is shown by the work of Hammick and Wilmut (1934, 1935), which is greater even than can be accounted for by the strain factors of Mumford and Phillips; thus for tetrabromo- and tetranitromethane the discrepancies are  $-16.7$  and  $-20.8$ , respectively, using the Sugden equivalents, and  $-11.6$  and  $-16.9$  when the strain constants are included. With carbon tetrachloride and various tri-substituted methanes the anomalies are, on the other hand, quite small.

A serious abnormality in connection with parachors has been brought to light by the study of a series of dialkyl sulphide derivatives of palladous chloride, having the general formula  $(\text{R}_2\text{S})_2\text{PdCl}_2$ . The results in Table XIX. were obtained by Mann

TABLE XIX. *Parachor of Palladium in Dialkyl Sulphide Derivatives :  $(\text{R}_2\text{S})_2\text{PdCl}_2$*

Alkyl Group (R).	[P] Obs.	Atomic Parachor of Pd.
Methyl . . .	463	36
Ethyl . . .	613	27
<i>n</i> -Propyl . . .	760	16
<i>n</i> -Butyl . . .	906	4
<i>n</i> -Amyl . . .	1,054	- 7

and Purdie (1935), the parachor equivalent for palladium, given in the last column, was obtained by subtracting from the observed parachors the known atomic contributions of all the other atoms



present; in this computation the revised values mentioned in the footnote on p. 105 were used.

By extrapolation of the measured parachors to a carbon-free compound the parachor equivalent of palladium is found to be 55–60, which is the correct order for its position in the periodic table. It is remarkable, however, that the apparent atomic parachors in Table XIX. decrease with increasing complexity of the compound studied; similar results were obtained with arsenic and phosphorus derivatives of palladium. The anomaly might be explained if the parachor equivalent for the  $\text{CH}_2$  group actually used, viz., 39.6, were about 2.3 units too high, but a value as low as 37.3 is quite incompatible with many other observations. Further, it has been found with a series of mercury mercaptides,  $\text{Hg}(\text{SR})_2$ , where R is an alkyl group, that although the apparent atomic parachor of mercury decreases in a manner similar to that shown for palladium in Table XIX., a constant value is attained when R is a *n*-heptyl group; an error in the equivalent for the  $\text{CH}_2$  group would, of course, lead to a steady decrease of the mercury parachor. Mann and Purdie are of the opinion that in the organo-metallic compounds examined, and in others which will be mentioned later, the shapes of the molecules are such that they do not fit together compactly in the liquid state; a high inter-molecular compression is consequently required to maintain the constant surface tension implied by the parachor (p. 99), and the molecular volume is correspondingly low. When the organic part of the molecule grows to such dimensions that the metal is relatively unimportant the anomaly ceases and the parachor contribution of the metal atom becomes constant, as actually observed in the mercury mercaptides. Whatever the explanation, the results recorded above are certainly of great importance, since they serve to indicate the limitations of parachor additivity.

### THE PARACHORS OF MIXTURES

The possibility of determining parachors from measurements of surface tension and density of solutions instead of pure liquids was first suggested by Hammick and Andrew (1929), and has







good agreement has been obtained for solutions of carbon tetrachloride, *m*-xylene and cyclohexane in benzene, and for ethyl acetate in carbon tetrachloride.

**Abnormal Results.** Associated solutes, *e.g.*, ethyl alcohol, acetic acid and acetone give parachor values by the mixture method, both in non-associated solvents, *e.g.*, benzene, and in associated solvents, which are in excellent agreement with those observed for the pure liquids at the same temperature; the results are, of course, lower than the calculated parachors (see pp. 98, 123). The mixture method therefore appears to be applicable to substances of various types, as the mixture law may be obeyed with both associated and non-associated compounds. Strictly speaking, the law is only valid if the two pure components have the same surface tension (Semerano, 1932), and it was found by Hammick and Andrew that if the values differ by more than 7 dynes per cm. then  $[P]_x$  increased as  $x$  is increased. Under these conditions, however,  $[P]_x$  is a linear function of  $x$ , and if the graph is extrapolated to  $x = 1$ , the resulting value of  $[P]_x$  is in excellent agreement both with the calculated parachor and with that obtained from measurements on the pure liquid. An example of this type of behaviour is provided by solutions of nitrobenzene ( $\gamma = 42.87$ ) in benzene ( $\gamma = 28.23$ ) at  $25^\circ$ ; the experimental parachors are given in Table XXI.

TABLE XXI.—*Parachors of Solutions of Nitrobenzene in Benzene*

$x$	$D$	$\gamma$	$[P]_m$	$[P]_x$
0.2129	0.9517	30.26	215.9	249.0
0.3707	1.0070	31.99	223.8	252.0
0.4822	1.0435	33.15	229.6	253.7
0.6109	1.0860	35.24	236.8	255.7
0.7063	1.1130	36.51	242.6	257.4
1.0000	1.1988	42.87	264.5	(262.5)

The extrapolated value of  $[P]_x$  for  $x = 1$ , which corresponds to that of pure nitrobenzene, is 262.5; the experimental parachor



for the pure liquid is 264.5, and the calculated value is 264.1. Other instances of the same kind are nitrobenzene in carbon tetrachloride ( $\gamma = 26.1$ ), and nitromethane ( $\gamma = 35.8$ ), acetophenone ( $\gamma = 38.77$ ) and ethyl ether ( $\gamma = 16.47$ ) in benzene. The mixture method can, therefore, still be used to determine parachors even if the simple mixture law does not apply.

### APPLICATIONS OF THE PARACHOR

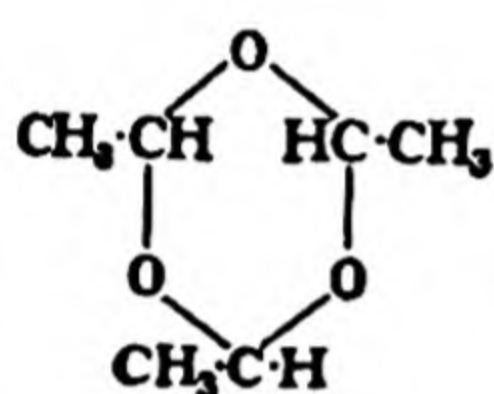
A number of interesting applications of the parachor have been made in connection with problems of chemical structure, and some of these will now be examined. In certain instances the conclusions to be drawn are still a matter for controversy, and these will be left until the more unequivocal cases have been discussed. The examples given all involve the fundamental assumption that the parachor is a truly additive property; to judge from the values obtained with a large number of compounds having definite structures and compositions there seems to be little doubt about this, although reference has been made to some apparent exceptions to the additive rule.

**The Structure of Benzene.** The parachor concept may be used in the following manner to throw light on the structure of the benzene ring. The total contribution of six atoms of carbon ( $6 \times 4.8$ ) and six atoms of hydrogen ( $6 \times 17.1$ ) is 131.4, and in addition there must be included that for a six-membered ring (6.1), making a total of 137.5, whereas the experimental value for benzene itself is 206.2. The deficiency of 68.7 is almost equal to the parachor equivalent of three double bonds ( $3 \times 23.2 = 69.6$ ), and so it appears that the parachor satisfies the requirements of the Kekulé formula. It is important to mention that the contribution for a six-membered ring is the same for benzenoid compounds as for cyclohexane derivatives, and so the parachor equivalent of 6.1 does not include any specific factor due to unsaturation; in the same way the parachor of the double bond is independent of the type of compound in which it occurs, and there appears to be no special effect due to conjugation. It seems, therefore, that the arguments favour the Kekulé

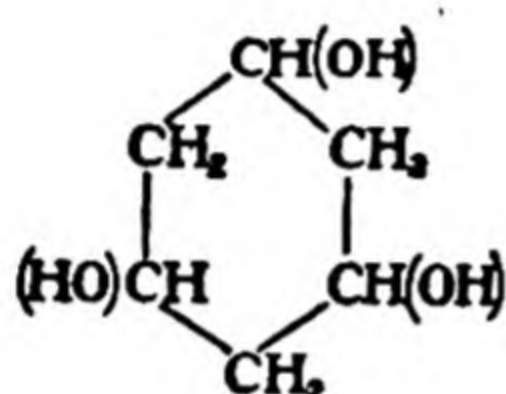


structure for benzene, and that the resonance effect (p. 88), which affects the bond distances, apparently does not influence the parachor.

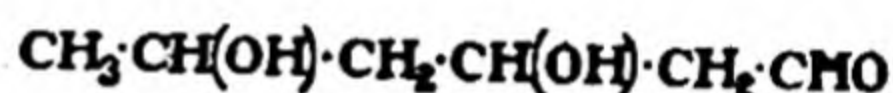
**Paraldehyde.** It is well established that acetaldehyde forms a polymer, paraldehyde, with the formula  $(C_2H_4O)_3$ , the parachor of which has been found to be 298.7; the value for acetaldehyde itself is 121.2, and for three molecules would be 363.6. The difference between 363.6 and 298.7 is 64.9, and corresponds very closely to the parachor equivalent of three double bonds (69.6); it appears then that in the paraldehyde molecule some or all of the double bonded  $>C=O$  groups, present in the original acetaldehyde, no longer exist. Three structures for the polymer are then possible



I  
[P] Cal 300.1



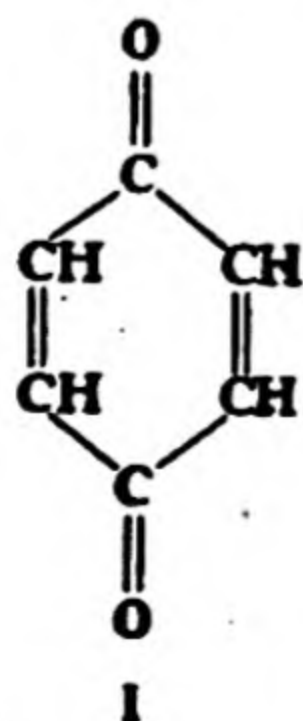
II  
[P] Cal 300.1



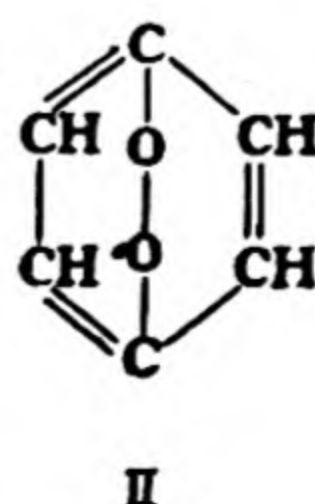
III  
[P] Cal. 317.2

with parachors of 300.1, 300.1 and 317.2 respectively. The experimental value of the parachor obviously eliminates formula III., but does not allow a choice to be made between I. and II.; purely chemical evidence must be used in order to arrive at a final decision.

**The Structure of Quinone.** Two different structures have been proposed to account for the properties of the *p*-quinones:



and



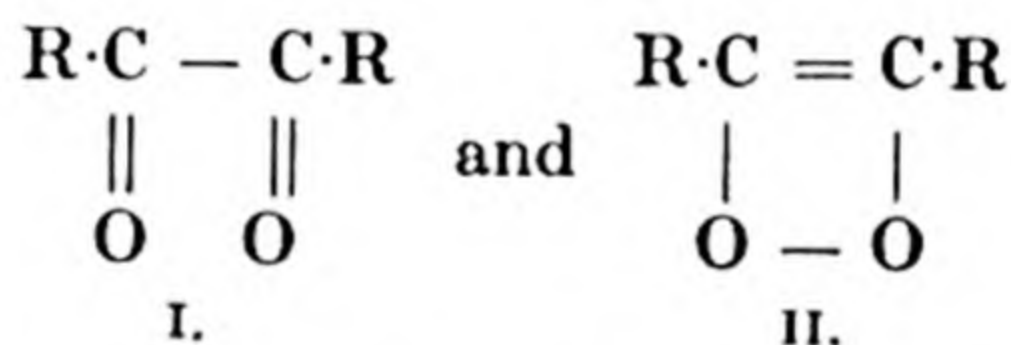
II



Although the majority of the chemical properties favour formula I. (diketone), some are better accounted for by formula II. (peroxide) and this is also in agreement with a number of physical properties, *e.g.*, absorption spectrum and heat of combustion. The parachor gives a very definite indication in favour of the diketone formula, which incidentally is the one preferred by most organic chemists; the experimental and calculated parachors are as follows:

	[P] obs.	[P] cal.	
		I.	II.
<i>p</i> -Benzoquinone . . .	236.8	236.1	219.0
<i>o</i> -Toluquinone . . .	272.0	275.1	258.0

**Diketones.** A somewhat similar problem is presented by benzil and its derivatives for which a diketone formula (I.) and a peroxide formula (II.) have been proposed:



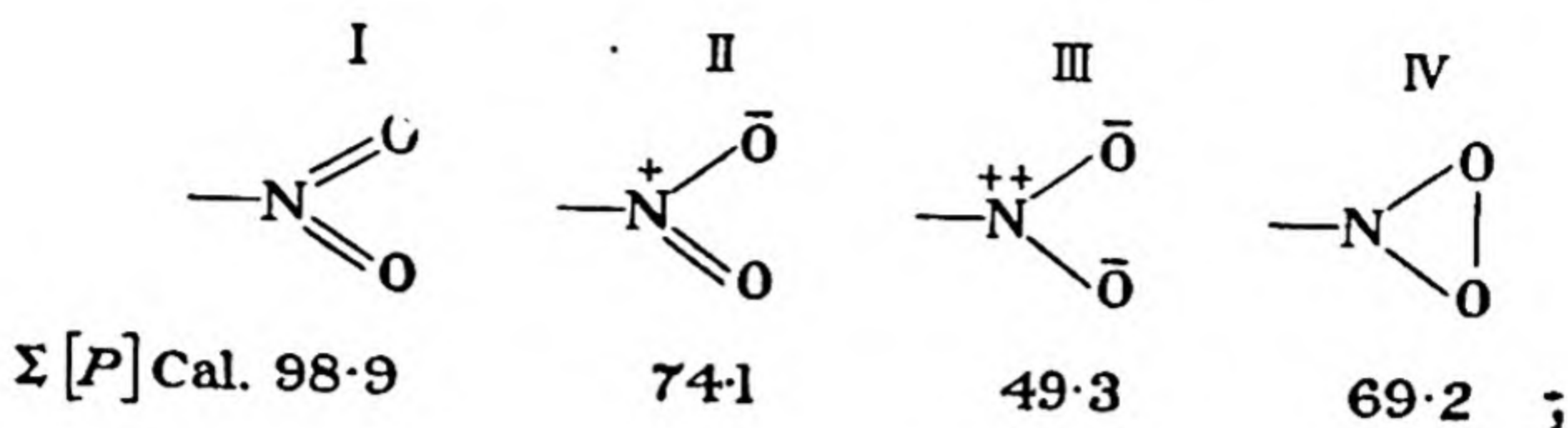
The following parachor values have been determined experimentally, and are compared with those calculated on the basis of the two alternative formulæ:

	[P] obs.	[P] cal.	
		I.	II.
Benzil . . . . .	480.8	476.0	464.4
2 : 2'-Dimethyl benzil.	596.8	594.0	582.4

These results indicate that in the liquid state, at least, benzil is a true diketone; it is possible, however, that structural changes may take place on solidification, as in some derivatives the colour of the liquid is different from that of the solid.

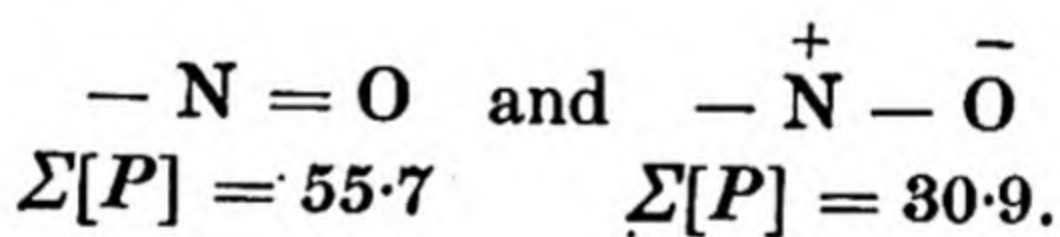
**Nitrogen Derivatives.** The parachor is also of interest in connection with the structure of certain nitrogen compounds, namely those containing the nitro-, nitroso-, azoxy-, diazo- and triazo-grouping. The nitro-group may be represented by one of the following structural formulæ:





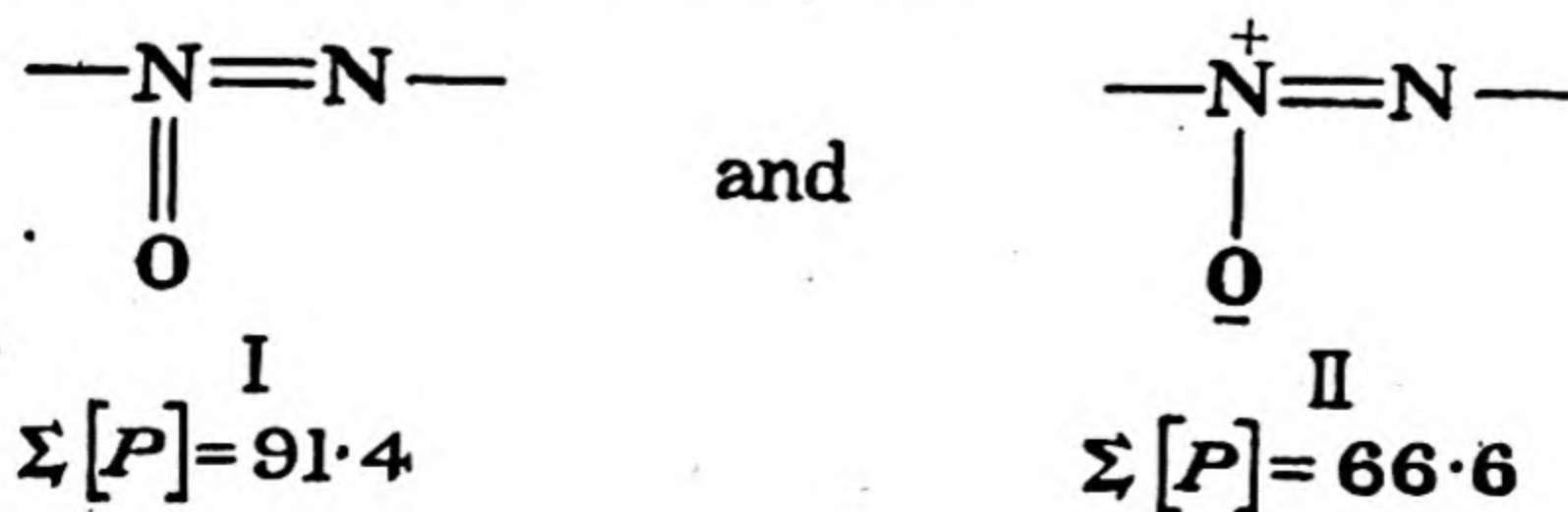
the parachors having been calculated from the known atomic and structural equivalents. The examination of a large number of compounds, both aliphatic and aromatic, and including nitrogen tetroxide, leads to an observed parachor of 73.0 for the nitro-group. This result establishes the accuracy of formula II., which is incidentally in best agreement with the chemical and physical properties of compounds containing this grouping (cf. p. 34). The parachor for the  $\text{—NO}_2$  portion of ethyl nitrate is found to be 74.5, and so the structure must presumably be the same as in nitro-compounds.

Since the nitro-group has one double bond and one semi-polar bond the question arises as to which of these is retained in nitroso-compounds; in other words two alternative formulæ are possible for the nitroso-group:



The mean value for the parachor of the  $\text{—NO}$  group determined from measurements on nitrosyl chloride, nitrosamines and alkyl nitrites is so close to 55 as to render quite certain the accuracy of the  $\text{—N}=\text{O}$  structure.

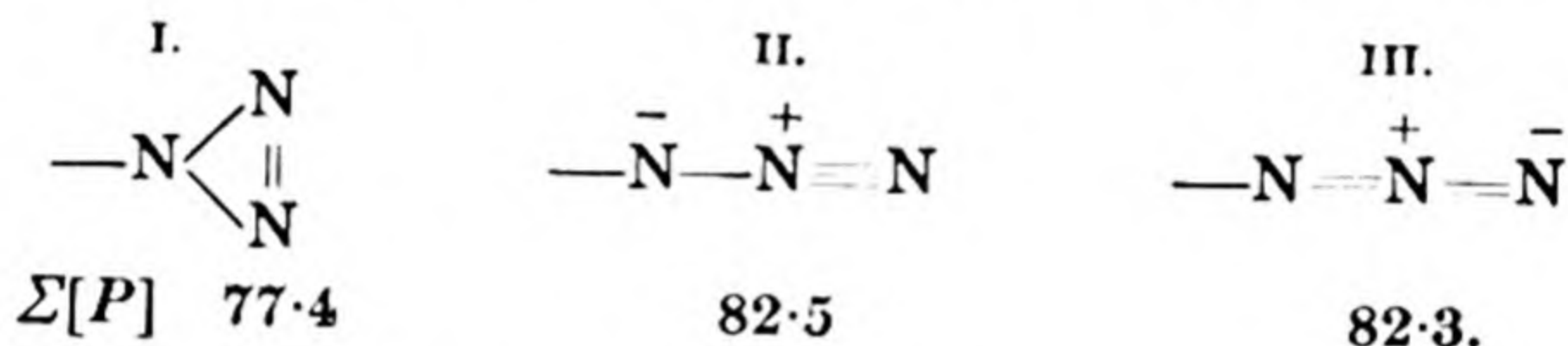
The azoxy-group may be represented in two ways, one of which is in accordance with older views on valency (I.), and the other is based on electronic theories; they are





The experimental parachors of azoxy-compounds are very close to the calculated value for formula II.; thus the parachor of azoxybenzene is 444.7 of which 380.0 is due to the two benzene nuclei, leaving 64.6 for the azoxy-grouping.

Both cyclic and straight-chain formulæ have been suggested, from time to time, for the triazo-group, and the various possibilities, excluding those which are rendered improbable by requiring penta-covalent nitrogen, may be represented as follows :



Lindemann and Thiele (1928) have examined a number of compounds containing the  $\text{—N}_3$  group and found the mean parachor contribution of the radical to be 77.2. This result apparently favours the ring structure I., although the differences between the three formulæ are not large. It may be noted, therefore, that X-ray examination of crystals of cyanuric azide (Knaggs, 1935) and electron-diffraction study of methyl azide vapour (Brockway and Pauling, 1933; see "Recent Advances in General Chemistry," Chapter V.) indicate that a linear structure is to be preferred. The bond distances suggest that resonance is occurring between the configurations II. and III. depicted above. Lindemann and his co-workers (1930) also concluded from parachor measurements that aliphatic diazo-compounds had a cyclic structure, but the electron-diffraction patterns of diazomethane vapour favour a linear formula (Boersch, 1935).

**The Isocyanide Structure.** Lindemann (1930) and Sidgwick (1930) have independently used parachor evidence to decide the much discussed structure of the isocyanide radical. The results in Table XXII., taken from the work of these authors, give the parachors of a number of isocyanides, together with the contribution of the  $\text{—NC}$  group determined by subtracting from the total the sum of the parachor equivalents of the remainder of the molecule.



TABLE XXII.—*Parachors of Isocyanides*

<i>Isocyanide.</i>	<i>[P] obs.</i>	<i>Parachor of — NC.</i>	<i>Mean.</i>
Methyl . . . .	122.1	66	66
Ethyl . . . .	164	69	
Phenyl . . . .	255.2	65	
<i>o</i> -Tolyl . . . .	292.9	63	
<i>p</i> -Tolyl . . . .	295	66	
<i>o</i> -Anisyl . . . .	314.1	65	
<i>p</i> -Anisyl . . . .	315	66	

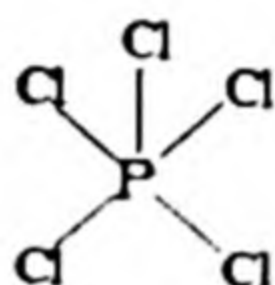
In the isocyanide group resonance probably occurs between the two possible structures  $-\text{N}=\text{C}$  and  $-\overset{+}{\text{N}}\equiv\overset{-}{\text{C}}$ . The parachor for the former is the sum of 12.5 for the nitrogen atom, 4.8 for the carbon atom, and 23.2 for the double bond, that is 40.5; for the second structure the calculated parachor equivalent is the sum of 12.5 and 4.8, as before, but now 46.6 must be added for a triple bond, and 1.6 subtracted for a semi-polar linkage, making a total of 62.3. The actual value shows that the  $-\overset{+}{\text{N}}\equiv\overset{-}{\text{C}}$  configuration predominates; this supports the conclusion arrived at from a study of dipole moments of isocyanides (see p. 176) and of the Raman effect (p. 251). The problem of the carbon monoxide structure is a similar one, since the formulæ  $\text{C}=\text{O}$  and  $\overset{-}{\text{C}}\equiv\overset{+}{\text{O}}$  are possible (p. 91); if the former were correct the parachor should be 48.0, and if the latter 69.6. The observed value of 61.6 favours the second structure as the main resonating state (see also p. 177).

### THE PARACHOR AND SINGLET LINKAGES

**The Pentachlorides of Group V.** Reference must now be made to the controversial subject of singlet linkages (p. 30), which has been raised by Sugden as a result of his parachor studies. If the observed parachors for phosphorus and antimony pentachlorides are compared with the values calculated, on the assumption that



all five chlorine atoms are attached to the central atom by ordinary single linkages, a discrepancy of 25 units is obtained ; the observed parachor is in each case lower than the calculated value. It appeared to Sugden, therefore, that the structure suggested was incorrect, especially as it involved the formation of a group of ten electrons around the phosphorus or antimony atom ; he consequently adopted the formula, previously suggested by Prideaux (1923), which satisfies the requirements of an electron octet but implies the presence of two singlet linkages, thus

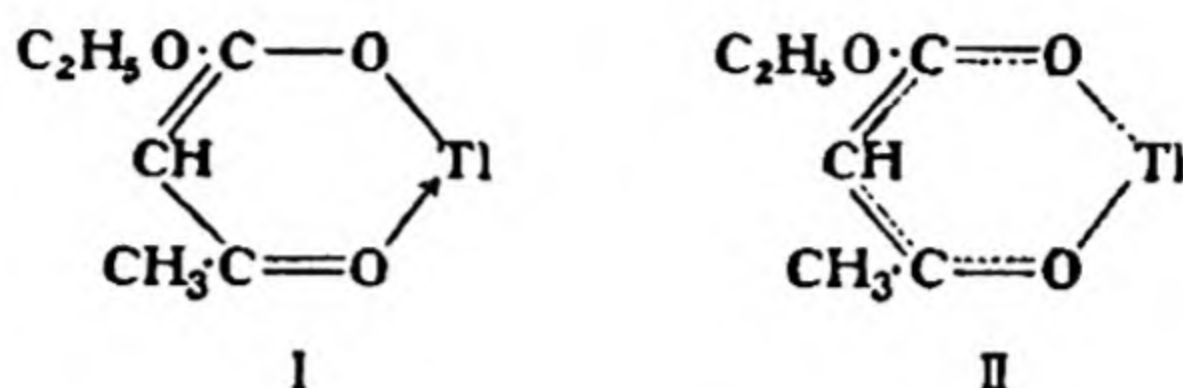


where the full lines represent the sharing of a pair of electrons and the dotted lines only one electron, *i.e.*, a singlet linkage. Sugden then suggested that the presence of such a bond *decreases* the parachor of a compound by 11.6 units ; this value is exactly half the increase resulting from the inclusion of a double bond. As it is supposed that in the pentachlorides under discussion each molecule contains two singlet linkages the corresponding parachor decrease should be 23.2 ; this is approximately equal to the mean difference observed (25 units) between the experimental and calculated values. A similar situation arises in connection with sulphur hexafluoride ; the observed parachor is 143.3 (Pearson and Robinson, 1933), whereas the additive value is about 198. If four of the fluorine atoms were joined to the sulphur by singlet linkages and two by ordinary electron-pair bonds, the octet would be maintained and the parachor difference explained. Certain aspects of the problem of singlet linkages have already been discussed in Chapter I., and the references to be made here deal only with the implications of parachor evidence.

**Chelate Compounds.** Perhaps the strongest argument presented in favour of the odd electron linkage is connected with the chelated metallic derivatives of diketones and similar compounds. Consider, for example, ethyl thalloacetoacetate, the observed parachor for which is 332.2 ; the formula favoured by Sidgwick involves



linkages consisting of ordinary electron pairs (I.), whereas Sugden's formula has a number of odd electron links, shown by dotted lines, as in II., thus



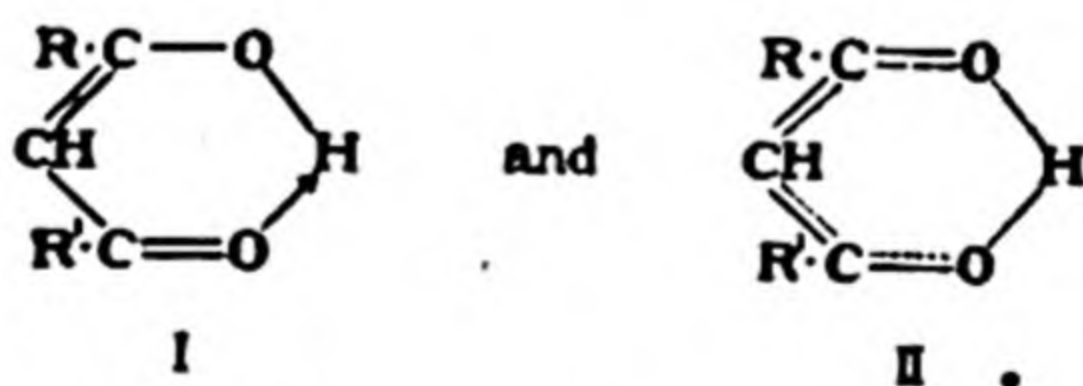
The sum of the parachor equivalents for formula I., excluding the thallium atom, is 293.6, whereas for formula II. it is 272.0; the atomic parachor of thallium would thus be 38.6, if formula I. were correct, or 60.2 if the other represented the structure of the compound. From an examination of other thallium compounds, *e.g.*, thallos ethoxide, in which the question of singlet linkages does not arise, the parachor equivalent of the thallium atom is found to be about 65; this result apparently supports the argument in favour of odd electron linkages. Sidgwick (1930) has, however, called attention to the fact that both the acetoacetate and the ethoxide of thallium are associated, and that in order to derive a parachor of approximately 60 from the complex formulæ it is necessary to assume that polymerisation results from the formation of duplet links between the thallium atoms in the ethoxide and singlets in the thalloacetoacetate; this difference of behaviour appears improbable. It must be realised, too, that thallium acetate and formate, from which Sugden derived a parachor equivalent of 65 for the thallium atom, have boiling points of 131° and 101° C., respectively, and so they are certainly not simple salts of the type [R·COO]Tl.

A study of beryllium acetylacetonate and propionylacetonate, and of basic beryllium propionate, seems to provide further evidence for the odd electron link. The atomic parachor for beryllium would be *negative* unless singlet linkages are assumed to be present in the molecule; adopting Sugden's formulæ, however, a positive parachor, ranging from 34.0 to 44.4 in the three compounds examined, may be obtained. Measurements on aluminium acetylacetonate and on aluminium bromide have given results of

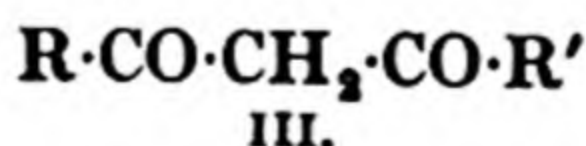


the same general nature ; they do not seem capable of explanation on the basis of the Sidgwick type of formula (I.), but the structures suggested by Sugden, with singlet linkages, yield reasonable values for the atomic parachor. Attention must, however, be called to the fact that the atomic parachor of palladium can be apparently negative for compounds wherein there is no question of singlet linkages (see Table XIX.). Compounds of the organo-metallic type evidently behave abnormally in the respect that their parachors are not strictly additive, and the more complex the organic part of the molecule, up to a point, the smaller is the apparent contribution of the metal atom. It is probable, therefore, as suggested by Mann and Purdie (1985), that in the compounds of thallium, beryllium and aluminium considered above, the variable or negative contribution of the metal atom to the parachor is to be expected. The fact that it occurs for the ordinary electron-pair formula is to be taken as evidence in favour of that rather than the one with singlet linkages.

It has been suggested that  $\beta$ -diketones have a cyclic, or chelated, structure involving co-ordinated hydrogen (p. 47) ; two formulæ are possible : one involving a normal hydrogen bond (I.), and the other with the hydrogen atom having two singlet linkages (II.), thus



The parachor equivalents for these two structures would be different, and so also would that for a straight chain formula (III.) :



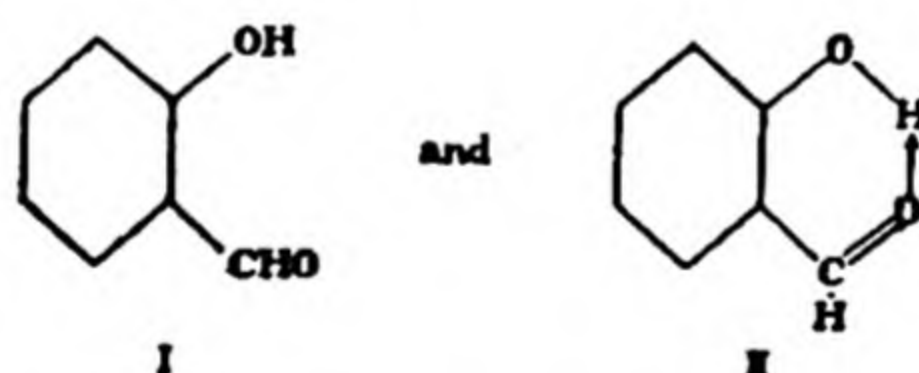
since it does not involve a ring. The experimental results for three diketones, and the values calculated for the three different possible structures are given in Table XXIII. ; allowance is made for the hydrogen bond as a co-ordinate linkage.



TABLE XXIII.—*Observed and Calculated Parachors of  $\beta$ -Diketones*

Substance.	Formula.	[P] obs.	I.	II.	III.
Acetyl acetone .	$C_5H_8O_2$	245.4	251.7	230.1	247.2
Propionyl acetone .	$C_6H_{10}O_2$	279.7	290.7	269.1	286.2
Benzoyl acetone .	$C_{10}H_{10}O_2$	382.4	385.6	364.1	381.1

**The Parachor and Covalency Increase.** These figures clearly eliminate formula II. as a possibility, and Sugden considers that they favour, as they apparently do, a straight chain structure for the  $\beta$ -diketones. Sidgwick (1925), however, has given good reason for believing that such, and similar, compounds do contain a chelate ring (p. 52), and he has published (1930) important parachor measurements on some *o*-substituted phenols, wherein there is little doubt that chelation does occur, which may help to clarify the situation. As an illustration may be taken *o*-hydroxybenzaldehyde, having the two possible formulæ I. (open structure) and II. (chelated structure) :



These two structures should correspond to different parachors, as in formula II. there is an additional six-membered ring (+ 6.1)

TABLE XXIV.—*Observed and Calculated Parachors of *o*-Phenols*

Substance.	[P] obs.	I.	Diff.	II.	Diff.
<i>o</i> -Nitrophenol .	274.7	283.0	−8.3	287.5	−12.8
<i>o</i> -Hydroxybenzaldehyde .	268.0	275.1	−7.1	279.6	−11.6
<i>o</i> -Vanillin .	325.1	334.1	−9.0	338.6	−13.5
Methyl salicylate .	322.1	330.9	−8.8	335.4	−13.3
				Mean	−12.8



and also a co-ordinate link ( $-1.6$ ). The experimental values for some *o*-phenols are given in Table XXIV., together with the parachors calculated on the basis of the two alternative formulæ.

From these figures it would appear at first sight that neither structure is correct, since the differences between observed and calculated results are, in both cases, much greater than are generally found. The evidence for the chelated structure is, however, very strong, and Sidgwick has made the important suggestion that the parachor anomaly found for the formula II., that is  $-12.8$  (Table XXIV., column six), is to be attributed to the increase of the effective covalency of hydrogen from one to two. Incidentally it may be mentioned that if the H of the  $-OH$  group in the *o*-phenols is replaced by a  $-CH_3$  group, and no chelation is possible, quite normal parachors are obtained. In general, Sidgwick proposes, therefore, to discard the idea of singlet linkages, and consequently the parachor equivalent attributed to them, and to replace it by the view that each increase of one unit in covalency results in a *decrease* of  $12.8$  units in the parachor. The suggestion accounts immediately for the apparently anomalous results obtained for the parachors of phosphorus and antimony pentachlorides (p. 116); in each of these substances the covalency of the central atom is increased from three to five, and a decrease of  $2 \times 12.8 = 25.6$  might be expected in the parachor. This is very close to the observed value, and so an alternative explanation is provided for one of the results upon which the singlet linkage theory was based. Similar results are obtained with sulphur hexafluoride (p. 116); the calculated parachor, based on the atomic value for bivalent sulphur, is nearly 55 units too high. The allowance for the change in valency would be  $4 \times 12.8 = 51.2$ , which is very close to the observed discrepancy. The parachor of disulphur decafluoride,  $S_2F_{10}$ , can be accounted for in the same manner (Denbigh and Whytlaw-Gray, 1934).

To return to the problem of the structure of the  $\beta$ -diketones: in order to allow for the increase in the covalency of hydrogen in formula I. (p. 118), it is necessary to subtract  $12.8$  from the corresponding calculated parachors; the new results are then as follows:—



	Obs.	Cal.
Acetyl acetone . . .	245.4	238.9
Propionyl acetone . . .	279.7	277.9
Benzoyl acetone . . .	382.4	372.8

The agreement for propionyl acetone is good, allowing for the fact that about 20 per cent. of the ketone will remain in the straight chain enolic form; the calculated results for the other cases are low, but it is not known to what extent the resonance effect which causes the chelation (cf. p. 94) may influence the parachor.

**Parachor Defects.** Sidgwick and Barkworth (1931) have collected, from their own observations and from the measurements of Lowry and Gilbert (1929), Sugden *et al.* (1929, 1930), and Simons (1930), the parachor defects in various compounds which Sugden would attribute to singlet linkages and Sidgwick regards as due to the increase of two units in the covalency of the element. The results, including a recent value for sulphur, are as follows:—

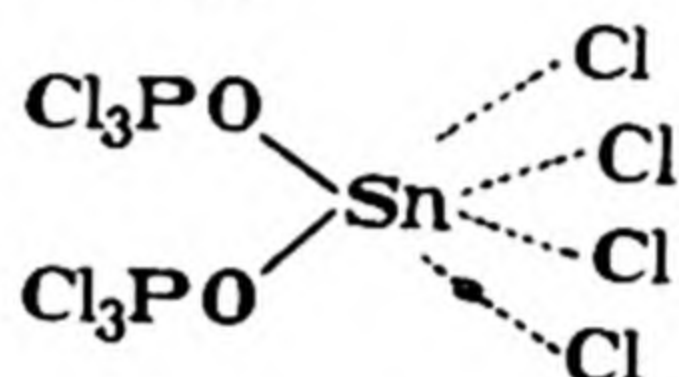
P	S	
26.7	27	
As	Se	
26.2 (calc.) [Diff. 3.7]	22.5	
Sb	Te	I
25.7 [Diff. 3.7]	22.0 [Diff. 4.7]	17.3

There is evidently a type of periodicity in these defects, and the values decrease, as might be expected, with increasing size of the atom. In a study of the addition compounds of boron trifluoride with various ethers and esters (see p. 37), Sugden and Waloff (1932) found good agreement between observed and calculated parachors, although the covalency of the boron was increased from three to four in these substances. They regard this as evidence against Sidgwick's theory that there is a decrease in the parachor as a result of an increase of covalency; it should not be forgotten, however, that the case of boron may not be quite comparable with that of the other elements. With boron the electron group is increased from the unstable sextet to the stable octet, whereas in the elements for which Sidgwick quotes the parachor defects the electron group is initially stable, viz., two for

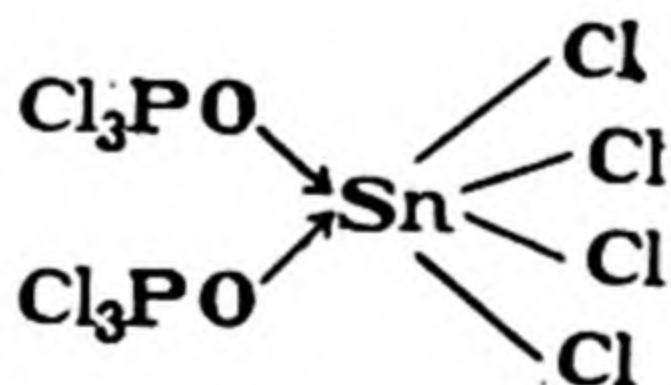


hydrogen, or eight for the other elements, and the increase of covalency results in the addition of further electrons.

In his discussion of singlet linkages Sugden includes the case of the molecular compound between stannic chloride and phosphorus oxychloride, viz.,  $\text{SnCl}_4 \cdot 2\text{POCl}_3$ . If the view is rigidly held that the outer sphere of the tin atom cannot contain more than eight electrons, then only three formulæ appear to be reasonably possible; two of these involve an ionised chlorine, and so must be ruled out immediately as the substance has all the properties of a completely covalent compound. The third remaining possibility is one involving singlet linkages:



for which the calculated parachor is 665.4, compared with the observed value of 689.7. In order to account for this marked anomaly Sugden assumes that the solid has the suggested structure, but that in the liquid, used of course in parachor measurements, partial dissociation has occurred into stannic chloride and phosphorus oxychloride. On the other hand, if the possibility is admitted that the outer electron group of tin may increase up to twelve, as it probably does in the stannichlorides where the covalency is six, the additive compound under discussion may be formulated



Allowing for the fact that the covalency of the tin atom is increased from four to six, and the corresponding parachor defect of 25.6—estimated from the results of Sidgwick and Barkworth (p. 121)—is included, the calculated parachor for the molecular compound is 682; this is not very different from the observed value and may be considered as good as could be expected,



especially in view of the uncertainty as to the atomic parachor of tin (value used 58 ; observed values 55.6—60.7).

In reviewing the situation it appears that the parachor evidence for the singlet linkage is not as decisive as might have been hoped for, and until more convincing proof is available it would seem preferable to retain the idea of the equivalence of a shared duplet of electrons with a valency bond. It is not impossible, however, that with developments in wave mechanics the conventional ideas on the subject may have to be modified.

### THE PARACHORS OF ASSOCIATED LIQUIDS

For associated liquids the observed parachors are generally lower than the calculated values, and, as may be expected, since the factor of association decreases with increasing temperature, the anomaly decreases as the temperature is raised. In Table XXV. are given some values, taken from the compilation by Sugden, for three typical associated liquids, namely ethyl alcohol, acetic acid and dimethylamine.

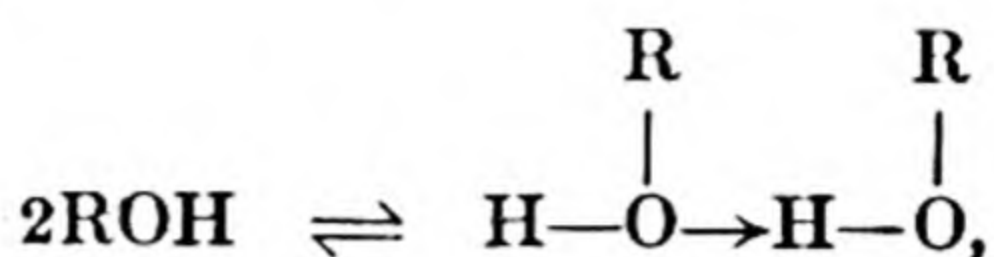
TABLE XXV.—*Parachors of Associated Liquids*

Ethyl Alcohol.		Acetic Acid.		Dimethylamine.	
$t^{\circ}$	[P]	$t^{\circ}$	[P]	$t^{\circ}$	[P]
—57	124.2	10	131.3	—78	133.4
—80	125.4	50	131.7	—50	134.1
0	126.4	100	132.2	—23	135.3
20	126.9	130	132.8	0	136.6
80	128.8	190	134.0	5	136.6
140	129.7	250	135.6		
200	131.0	280	137.0		
Calculated	132.2	Calculated	141.2	Calculated	141.8

Sidgwick (1930) has been able to account quantitatively for these anomalies on the basis of the view that an increase of covalency results in a parachor decrease. Suppose for example



that association between two molecules of a hydroxylic compound occurs as follows :—



then as a result of the association one co-ordinate link (parachor — 1·6) is produced and there is an increase of one in the covalency of a hydrogen atom (parachor — 12·8). The parachor decrease should thus be 14·4 divided between two molecules, that is 7·2 per molecule. In the same way the formation of a triple polymeride would mean a decrease of  $2 \times 14·4 = 28·8$  in the parachor, divided between three molecules, or 9·6 per molecule. At low temperatures the observed parachor anomalies (see Table XXV.) are between 8 and 10, indicating the presence mainly of double and triple molecules; similar values are obtained for methyl alcohol, various fatty acids and amines, nitric acid and sulphuric acid. This conclusion is in harmony with other views concerning the factor of association of hydroxylic and other compounds. As the temperature is raised the extent of association decreases and so, of course, must the parachor anomaly which it produces.

A number of associated liquids, however, unexpectedly yield normal parachors. There is reason to believe, for example, that *m*- and *p*-phenolic compounds are associated, yet they have quite normal parachors. Phenol itself is probably less associated than some of its *m*- and *p*-derivatives, yet it shows an expected anomaly of — 4·8 in its parachor at 49·6°, and one of — 2·3 at 147·5°, and so the absence of the anomaly in its derivatives is very remarkable. Water is also quite definitely associated at ordinary temperatures, but the observed parachor at 20° is only 1·5 smaller than the calculated value; the difference between the two values increases slightly, instead of decreasing, as the temperature is raised and is — 2·1 at 100° C. It has been seen (p. 95) that the association in compounds of this type is due to a particular form of resonance involving hydrogen, and nothing is definitely known of the effect this is likely to have on the parachor. It may in some manner account for the observed anomalies.



## THE PARACHORS OF ELEMENTS

The parachors of some elements, measured on the elements themselves, show anomalies, whereas for others the values are in agreement with those determined from their atomic parachors in compounds. Some examples of "normal" and "abnormal" elements are given in Table XXVI.

 TABLE XXVI.—*Parachors of Elements*

Normal.			Abnormal.		
Substance.	[P] obs.	[P] cal.	Substance.	[P] obs.	[P] cal.
Hydrogen .	35.2	34.2	Nitrogen .	60.4	71.4
Chlorine .	111.5	108.3	Oxygen .	54.0	63.2
Bromine .	132.1	136.0	Aluminium .	55.0	38.6
Mercury .	69.4	68.7	Tin .	85.1	54.8
			Lead .	91.4	76.2

Sugden suggests that the anomalous results when negative are due to association, but when positive to the presence of doubly and triply linked molecules in the liquid. There is no certainty, however, that the parachor of an element should be the same in the combined and uncombined states.

## REFERENCES

- ATEN. *Rec. trav. chim.*, 1935, 54, 666.  
 BARONI. *Atti R. Accad. Lincei.*, 1931, 14, 28.  
 BARRICK, DRAKE and LOCHTE. *J. Amer. Chem. Soc.*, 1936, 58, 160.  
 BECK, MACBETH and PENNYCUICK. *J. Chem. Soc.*, 1932, 2258.  
 BHATNAGAR and SINGH. *J. Indian Chem. Soc.*, 1929, 6, 263; 1930, 7, 663.  
 BUEHLER *et al.* *J. Amer. Chem. Soc.*, 1932, 54, 2398; 1934, 56, 2061.  
 CHEESMAN. *J. Chem. Soc.*, 1930, 35; 1932, 889.  
 DENBIGH and WHYTLAW-GRAY. *Ibid.*, 1934, 1346.  
 ELLIS. *Ibid.*, 1932, 1697.  
 GODCHOT and CAUGUIL. *Compt. rend.*, 1931, 192, 1560.  
 HAMMICK *et al.* *J. Chem. Soc.*, 1929, 754; 1930, 1876; 1934, 32; 1935, 207.  
 HUNTER and SAMUEL. *Rec. trav. chim.*, 1935, 54, 114.  
 JOHNSON. *Ber.*, 1932, 65, 294.  
 LINDEMANN *et al.* *Ibid.*, 1928, 61, 1529; 1930, 63, 702, 715, 1650.  
 LOWRY and GILBERT. *J. Chem. Soc.*, 1929, 2087.  
 LOWRY and JESSOP. *Ibid.*, 1930, 1005.  
 MACLEOD. *Trans. Faraday Soc.*, 1923, 19, 88.



- MANN and PURDIE. *J. Chem. Soc.*, 1935, 1549.  
MUMFORD and PHILLIPS. *Ibid.*, 1928, 155 ; 1929, 2112 ; *Ber.*, 1930, 63, 1818.  
PERSHKE. *Ibid.*, 1929, 62, 3054.  
RAY. *J. Ind. Chem. Soc.*, 1934, 11, 671, 843 ; 1935, 12, 780.  
ROBINSON *et al.* *J. Chem. Soc.*, 1932, 972 ; 1933, 1427 ; 1934, 736.  
SEMERIA and RIBOTTI-LISSONE. *Gazz.*, 1930, 60, 862.  
SIDGWICK *et al.* *J. Chem. Soc.*, 1925, 127, 907 ; 1929, 1108 ; 1930, 1461, 2027 ; 1931, 807 ; *J. Amer. Chem. Soc.*, 1932, 54, 948.  
SIMONS. *Ibid.*, 1930, 52, 3488.  
SIPPEL. *Ber.*, 1930, 63, 2185.  
SPEAKMAN. *Nature*, 1932, 129, 244.  
SUGDEN *et al.* *J. Chem. Soc.*, 1924, 125, 82, 1177 ; 1925, 127, 1525, 1868 ; 1927, 189, 1173, 1780, 1786 ; 1928, 263, 410, 989, 1055 ; 1929, 316, 989, 1058, 1291, 1298 ; 1930, 2572 ; 1932, 760, 1492 ; "The Parachor and Valency," 1930\*.  
VOGEL. *J. Chem. Soc.*, 1934, 333, 1758.

\* Review papers and books, wherein further references are to be found, are marked by an asterisk.



## CHAPTER III

### DIPOLE MOMENTS

**The Mosotti-Clausius Equation.** Suppose two similar conducting plates which are uniformly electrically charged are placed parallel to one another; the intensity of the electrical field in the space enclosed by the plates will depend on the medium it contains. If a vacuum separates the plates, for example, the field strength may be designated by  $E_0$  for a given charge, but when a uniform material substance is present this intensity is reduced to  $E$  for the same charge. The ratio of  $E_0$  to  $E$  is a constant, called the dielectric constant  $\epsilon$  of the medium between the charged plates, thus

$$\frac{E_0}{E} = \epsilon \quad . \quad . \quad (i.)$$

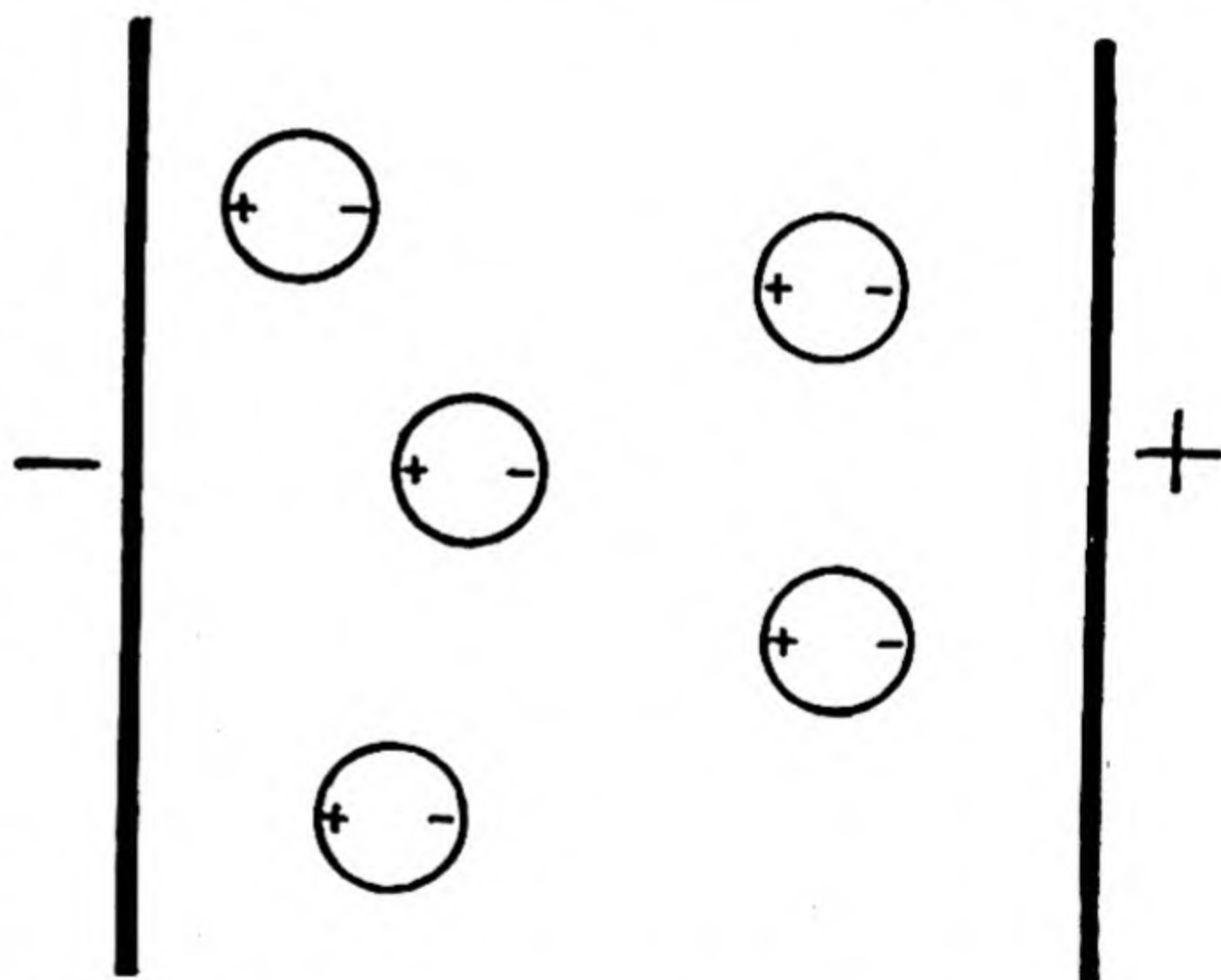


FIG. 2.—Induced charges in molecules, causing distortion polarisation, resulting from the presence of charged plates.

In order to account for the reduction in field strength it has been assumed that the molecules of the medium act as perfect conductors, and that the charged plates cause charges to be induced in these molecules (Fig. 2). This implies that the electrical field causes a displacement of the positive and negative charges, which in the normal uncharged molecules are supposed to be distributed uniformly, so that the molecules become "polarised." In other words, a molecule although originally non-polar, that is the



“centres of gravity” of the positive and negative charges coincide, is distorted in an electrical field, so that it becomes an induced “dipole” or “electrical duplet.” These induced charges are, of course, opposite in direction to those of the charged plates, so that the former set up an electrical field which opposes, and so reduces that of the latter; the value of the field intensity  $E_0$  is thus reduced to  $E$ . On the basis of this theory Mosotti (1850) and Clausius (1879) deduced mathematically an equation which may be written in the form

$$\frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d} = \frac{4\pi N}{3} \gamma \quad \dots \dots \dots (ii.)$$

where  $\epsilon$  is the dielectric constant, and  $M$  the molecular weight of the substance constituting the medium,  $d$  its density and  $N$  the Avogadro number ( $6.06 \times 10^{23}$ );  $\gamma$  is a constant for the medium and is called the “molecular polarisability” due to induced dipoles. The quantity  $\gamma$  is defined in terms of the equation

$$m = \gamma F \quad \dots \dots \dots (iii.)$$

where  $m$  is the electrical moment induced in a molecule by a field of strength  $F$ ; this moment,  $m$ , is equal to the product of the induced charge and the displacement of the centres of the charges within the molecule. The Clausius-Mosotti equation (ii.) may be regarded as applicable to all states of matter.

**Molar Polarisation.** The term  $\frac{4\pi N}{3} \gamma$  on the right-hand side of equation (ii.) is called the “molar polarisation” due to distortion, or to induced dipoles, and may be given the symbol  $P_D$ . By inserting the known values for the Avogadro number and for  $\pi$  the expression for  $P_D$  reduces to  $2.54 \times 10^{24} \gamma$ , that is

$$P_D = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d} = 2.54 \times 10^{24} \gamma \quad \dots \dots \dots (iv.)$$

The molar polarisation  $P_D$  of any substance may be calculated from the dielectric constant and its molecular weight and density. Since the dielectric constant is not easily determined, especially as the values for gases are not far from unity, an alter-







value of  $n$  may be determined by two or three measurements of  $n$  at known wavelengths  $\lambda$  within the visible region ; by assuming that the value is applicable on extrapolation to larger wavelengths the required  $n_\infty$  may be calculated.

**Electron and Atom Polarisation.** It has been pointed out by Ebert (1924) that although the refractive index may be extrapolated in this manner to the value for long waves, it is calculated directly from measurements made with high-frequency radiations, *i.e.*, visible light, which can only displace electrons : the heavier nuclei remaining unaffected. The molar polarisation given by

$$\frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d}$$

even when  $n$  is extrapolated to long wavelengths, does not give the whole of the polarisation, but only the "electron polarisation"; this quantity is given the symbol  $P_E$ . In order to determine the whole of the displacement, or distortion, polarisation it is necessary actually to measure the refractive index with radiations of long wavelength, *e.g.*, infra-red ; vibrations with comparatively low frequency are able to influence and displace the nuclei, which carry the atomic mass, as well as the electrons. The difference between this total polarisation due to displacement  $P_D$  and the electron polarisation  $P_E$  is called the "atom polarisation," and given the symbol  $P_A$ . In many instances  $P_A$  is only a very small proportion of  $P_D$  and so very little error results in calculating  $P_D$  from measurements of  $n$  made in visible light. It is, however, not always possible to neglect  $P_A$  : with liquid water, for example,  $n$  is 1.33 for ordinary light, and the extrapolated value  $n_\infty$  is not very different ; hence

$$P_E = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} = 8.7.$$

The infra-red refractive index of water  $n_r$  is 2.0, and so

$$P_D = P_A + P_E = \frac{n_r^2 - 1}{n_r^2 + 2} \cdot \frac{M}{d} = 9.0 ;$$

therefore  $P_A = 5.8$ . The value of  $P_A$  thus forms a considerable part of  $P_D$ , and the polarisation calculated from the value of  $n$  in



visible light, or even extrapolated from this value, gives less than half of the total displacement polarisation. In discussing the division of  $P_D$  into  $P_A$  and  $P_E$  the important fact should not be forgotten that the original Mosotti-Clausius equation involving the *dielectric constant* always gives the *total* polarisation irrespective of how it is divided up; this method of determining the polarisation is always the more reliable.

### THE DIELECTRIC CONSTANT AND MOLECULAR RADIUS

The refractive index of a gas or vapour is generally very close to unity, and so the polarisation equation may be simplified thus

$$P_D = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d} \approx \frac{\epsilon - 1}{8} \cdot \frac{M}{d} \quad \dots \quad (\text{ix.})$$

For a perfect gas the fraction  $M/d$  is a constant, equal to  $22.4 \times 10^3$  c.c. at  $0^\circ \text{C.}$  and 1 atm. pressure, independent of the nature of the gas. As already shown

$$P_D = 2.54 \times 10^{24} \gamma \quad \dots \quad (\text{vi.})$$

hence

$$\gamma = 2.94 \times 10^{-21} (\epsilon_0 - 1) \quad \dots \quad (\text{x.})$$

where  $\epsilon_0$  is the dielectric constant at  $0^\circ \text{C.}$  and 1 atm. pressure. For a conducting sphere of radius  $r$ , it can be shown that the induced electric moment ( $m$ ) in a field of intensity  $F$  is given by

$$m = r^3 F \quad \dots \quad (\text{xi.})$$

Since  $m = \gamma F$ , (equation (iii)), it follows that

$$\gamma = r^3 \quad \dots \quad (\text{xii.})$$

and finally that

$$r^3 = 2.94 \times 10^{-21} (\epsilon_0 - 1) \quad \dots \quad (\text{xiii.})$$

It is possible, therefore, to determine the approximate radius of a molecule, provided that the dielectric constant is known, by assuming it to be a uniform conducting sphere to which this equation is applicable.

In Table XXVII. some of the values for molecular radii of gaseous molecules calculated in this manner are compared with those obtained by other methods. The first column of figures gives  $(\epsilon_0 - 1) \times 10^3$  as obtained from direct measurement of the



dielectric constant, whereas in the second column there are the values for  $(n^2 - 1) \times 10^3$ ,  $n$  being the refractive index extrapolated to infinite wavelength; if the Maxwell equation,  $n^2 = \epsilon$ , applies these results should be equal. The values of  $r$  determined from  $\epsilon_0$  by means of equation (xiii.) are quoted in the third column ( $r_\epsilon$ ), whereas the values from  $n^2$  are given in the fourth column ( $r_n$ ). The molecular radii calculated from viscosity measurements ( $r_v$ ), and from the van der Waals equation ( $r_b$ ) on the assumption that the volume of a molecule is equal to  $\frac{1}{4}b$ , are in the fifth and sixth columns, respectively.

TABLE XXVII

*Molecular Radii from Dielectric Constant and Other Measurements*

Gas.	$(\epsilon_0 - 1) \times 10^3$	$(n^2 - 1) \times 10^3$	Molecular Radius in $10^{-8}$ cm. Units.			
			$r_\epsilon$	$r_n$	$r_v$	$r_b$
Hydrogen . .	0.264	0.272	0.92	0.93	1.09	1.25
Argon . . .	—	0.560	—	1.18	1.43	1.46
Chlorine . .	—	1.436	—	1.62	1.85	1.65
Nitrogen . .	0.581	0.581	1.20	1.20	1.55	1.42
Ethylene . .	1.25	1.35	1.54	1.58	2.27	1.30
Ammonia . .	7.18	0.75	2.76	1.30	1.45	1.14
Ethyl chloride .	15.4	—	3.56	—	—	1.51
Water . . .	4.0	0.51	2.27	1.14	—	1.08
Methyl alcohol .	6.0	1.20	2.60	1.52	—	1.45

An examination of the results given indicates that for the first five gases mentioned the agreement between  $\epsilon_0$  and  $n^2$ , wherever the data are available, is quite good, and at the same time the molecular radii determined from these values are quite reasonable, in view of the assumptions made, when compared with the results obtained from viscosity and compressibility (van der Waals' data). For the last four substances mentioned in the table, however, not all of these agreements are to be observed. In the first place  $\epsilon_0$  is considerably greater than  $n^2$  and although the radii calculated from the equation (similar to equation (xiii.) )

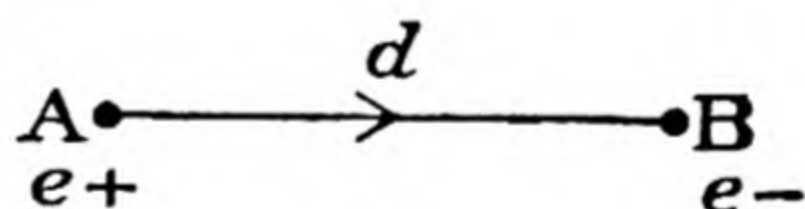
$$r^3 = 2.94 \times 10^{-21} (n^2 - 1) \quad . \quad . \quad . \quad \text{(xiv.)}$$



are reasonably satisfactory, those obtained from equation (xiii.) itself are undoubtedly much too large. Incidentally it has been noted that with substances which behave abnormally in this manner the molar polarisation varies with temperature, whereas according to the Mosotti-Clausius equation it should be constant.

## PERMANENT MOLECULAR DIPOLES

**Orientation Polarisation.** In discussing the exceptional behaviour of gases like ammonia and methyl alcohol vapour Debye (1912) pointed out that in the Mosotti-Clausius deduction no account had been taken of the possibility that the molecules of the medium might be *permanent* dipoles ; if this were so they would exert an effect on an electric field which would be superimposed on to that due to the induced dipoles. Any polar molecule, that is one in which the mean electrical centres of positive and negative charges do not coincide, will have such a permanent dipole. If A and B represent the normal electrical centres of positive and negative charges, both of which are equal to  $e$  since the molecule as a whole is electrically neutral,



then the "dipole moment" ( $\mu$ ) of the molecule is equal to  $de$ , where  $d$  is the distance between A and B. In the ordinary way the molecules, even of a polar substance, will be arranged in all possible directions so that the net electrical field due to them is zero ; if placed between two charged plates, however, they will tend to orient themselves so that the positive end of the permanent dipole is towards the negatively charged plate, and *vice versa*. These dipoles, therefore, will have the effect of opposing and so reducing the strength of the electrical field between the charged plates. If by some means the molecules were fixed and unable to orient themselves in the field they would be unable to oppose the intensity of the latter ; the polarisation resulting from the presence of permanent dipoles is, therefore, called "orientation polarisation," and given the symbol  $P_{\mu}$ .



**Permanent Dipole Moment.** On the basis of these considerations Debye, following Langevin's treatment of magnetic moments, showed that the *total* polarisation  $P (= P_A + P_E + P_\mu)$ , which is the quantity obtained from the Mosotti-Clausius equation, was given by the relationship

$$\frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d} = P = \frac{4\pi N}{3} \gamma + \frac{4\pi N}{3} \cdot \frac{\mu^2}{3kT} \quad \text{. . . (xv.)}$$

where  $\mu$  is the moment of the permanent dipole,  $k$  is the Boltzmann constant, that is  $R/N$ , the gas constant per single molecule, and  $T$  is the absolute temperature. The distortion polarisation  $P_D$ , which is equal to the sum of the electron and atom polarisations ( $P_A + P_E$ ), is still given by the equation

$$P_D = P_A + P_E = \frac{4\pi N}{3} \gamma \quad \text{. . . . . (xvi.)}$$

and, as before,

$$P_E = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} \quad \text{. . . (xyii.)}$$

where  $n$  is extrapolated from observations with visible light. It follows, therefore, that the orientation polarisation is as follows:

$$P_\mu = \frac{4\pi N}{3} \cdot \frac{\mu^2}{3kT} \quad \text{. . . . . (xviii.)}$$

It may be noted that this deduction was based by Debye on classical mechanics; the older quantum theory gave a value of  $2kT$  instead of  $3kT$ , but the latter has now been restored by the new quantum mechanics.

From the definition of  $P_\mu$  it is seen that the value depends on the temperature; as the temperature is raised the increased kinetic energy of the molecules will decrease the tendency for them to become oriented, so that the value of  $P_\mu$ , as equation (xviii.) implies, decreases as the temperature is increased.

It has already been mentioned (p. 188) that the gases which do not give agreement with the relationship  $\epsilon_0 = n^2$ , show variations in the polarisation with temperature. Clearly the molecules of these gases constitute permanent dipoles, as might be expected from an examination of their structures. The presence of the



dipole makes the total polarisation, and hence the value of the dielectric constant  $\epsilon$ , greater than would be expected if distortion polarisation alone occurred in the electrical field. This accounts for the fact that the molecular radius, calculated on the assumption that equation (xiii.) applies, is larger than the true value. Since the use of  $n^2$  instead of  $\epsilon$  does give a close approximation to the distortion effect (equation (xvii.)) it is not surprising that even with the polar molecules a reasonably accurate value for the molecular radius may be calculated by means of equation (xiv.).

### POLARISATION AND PHYSICAL STATE

**Solid and Liquid States.** Another interesting aspect of the question of orientation polarisation is that in the solid state, apart from a small number of exceptional cases (Smyth and Hitchcock, 1932), the molecules remain almost rigidly fixed in the space lattice, so that no orientation in the direction of the electric field is possible. Under these conditions even a polar molecule will show no orientation polarisation, and there should thus be a marked difference between the total polarisation in the liquid and solid states. For a non-polar substance, however, there is no orientation polarisation in any case, and so the difference in the two states should be small. This view is borne out in practice; benzene, for example, appears to be a good instance of a non-polar molecule, and the values for  $P$ , determined from dielectric constants, are 26.5 c.c.\* in the liquid state, and 26.9 c.c. in the solid state. It is interesting to mention, too, that the value of  $P_E$ , calculated from the refractive index, is 25.7 c.c., and so the sum of  $P_A$  and  $P_\mu$  is about 0.8; this is probably due entirely to the atom-distortion polarisation  $P_A$ , and benzene presumably has no permanent dipole moment.

Although this type of agreement is generally found for non-polar molecules, it appears that in some cases, *e.g.*, sulphur tetrachloride (Lowry and Jessop, 1930) and phosphorus pentachloride (Simons and Jessop, 1931; Lowry and Hofton, 1932), the polarisation is

\* An examination of the Mosotti-Clausius equation will show that molar polarisation must be expressed in volume units.



distinctly greater in the solid than in the liquid state; this is attributed either to distortion of the molecule by the lattice forces of the crystal (Simons) or to a change of molecular structure (Lowry).

With water, which is a polar substance, the total polarisations in the liquid and solid states are quite different; they have been found to be 17.5 c.c. for liquid water and 9.5 c.c. for ice, and the difference between these two values (8.0 c.c.) should be approximately equal to the orientation polarisation  $P_\mu$  for the water molecule. It has been seen (p. 130) that  $P_D (= P_A + P_E)$  for water, calculated from the infra-red refractive index, is 9.0, and so  $P_\mu = P - P_D = 17.5 - 9.0 = 8.5$  c.c., in good agreement with the expected value from the liquid-solid difference.

**Liquid and Vapour States.** It will be observed that in quoting the values of  $P_E$  determined from the Lorentz-Lorenz equation, no reference has been made to the physical state of the substance; as a matter of fact the electron polarisation, that is molecular refraction, is not only almost independent of the temperature, but it varies little with change of state. Table XXVIII. contains three examples which confirm this statement; they are for (a) a highly polar substance, water, (b) a slightly polar compound, chloroform, and (c) one which has no permanent moment, carbon disulphide.

TABLE XXVIII.—*Molar Refraction, or Electron Polarisation*

Substance.	Vapour.	Liquid.
Water . . . . .	3.72	3.71
Chloroform . . . . .	21.45	21.37
Carbon disulphide . . . . .	22.07	21.36

It will be observed from Table XXVIII. that the electron polarisations are greater in the vapour than the liquid phase; the difference although small is quite general and is to be anticipated from theoretical considerations of the optical anisotropy of the molecules (Raman and Krishnan, 1928; Goss, 1933).

The Debye equation (xv.) is applicable, strictly speaking, to



gases and, in a slightly modified form (*vide infra*), to dilute solutions of a polar substance in non-polar liquids. In concentrated solutions, or in a pure liquid, or even in a gas under high pressure, the dipolar molecules will tend to "associate" so as to minimise the effect of the external electric field (Fig. 3); the polarisation will thus

be less than would be expected from the value of the permanent polar moment of each separate molecule. The tendency for polar substances, *e.g.*, water and alcohols, to form associated molecules

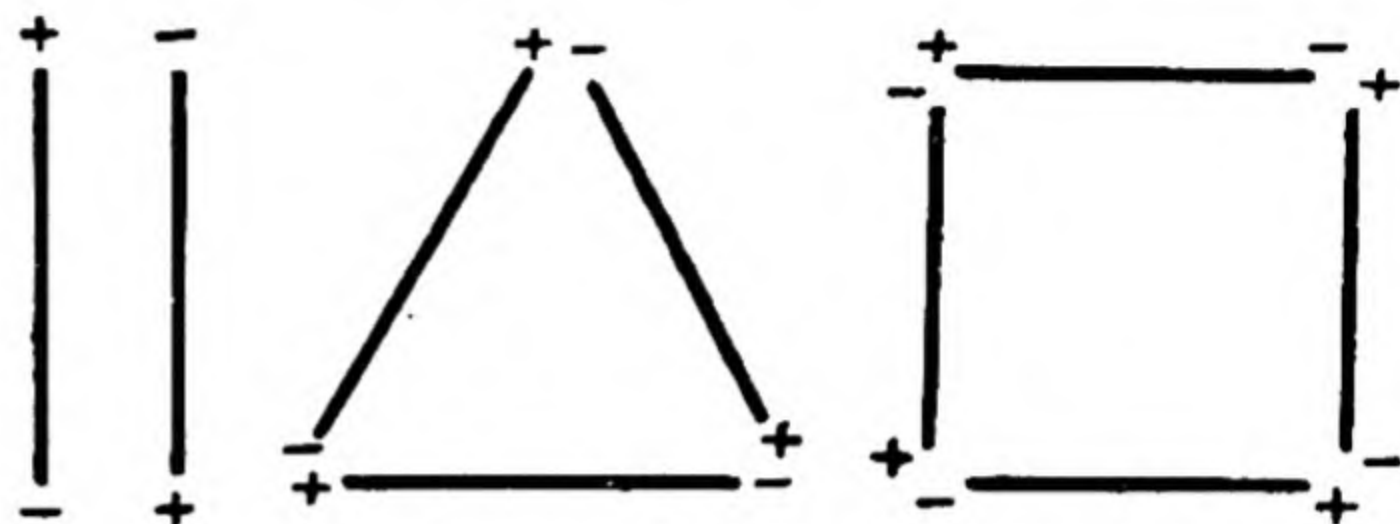


FIG. 3.—Dipole association, occurring in concentrated solutions, which tends to minimise the effect of the external electric field.

is, of course, well known, and the extent of association is known to decrease when vaporisation occurs. It follows, therefore, that for a molecule with a permanent dipole the total polarisation for the vapour should be greater than that of the liquid; the results in Table XXIX. bear out this anticipation.

TABLE XXIX.—*Sum of Atom and Orientation Polarisation*

State.	Water.	Methyl alcohol.	Ethyl alcohol.
Liquid . . .	13.8	28.8	39.2
Vapour . . .	56.3	54.7	54.9

Since  $P_A$  is comparatively small, and in any case probably does not vary with the physical state of the substance, the differences between the values quoted for liquid and gaseous states are to be attributed to changes in  $P_\mu$ . In making use of the Debye equation to study the dipole moments of various substances it is preferable to work with gases or with dilute solutions; if there is any marked variation of  $P_\mu$  with the concentration of the solution it is advisable to extrapolate the results to infinite dilution.



## THE DETERMINATION OF DIPOLE MOMENTS

**The Temperature Method.** In order to determine dipole moments experimentally, the Debye equation (xv.) is written in the form

$$P = a + \frac{b}{T} \quad \text{. . . . . (xix.)}$$

where  $a$  and  $b$  are constants for a given substance ; thus

$$a = \frac{4\pi N}{3} \gamma \quad \text{. . . . . (xix.a)}$$

and

$$b = \frac{4\pi N}{3} \cdot \frac{\mu^2}{3k} \quad \text{. . . . . (xix.b)}$$

Since  $N$  is  $6.06 \times 10^{23}$ , and  $k$  is  $1.37 \times 10^{-16}$  ergs per degree, it can be shown that

$$\mu = 0.0127 \sqrt{b} \times 10^{-18} \text{ electrostatic units} \quad \text{. . (xx.)}$$

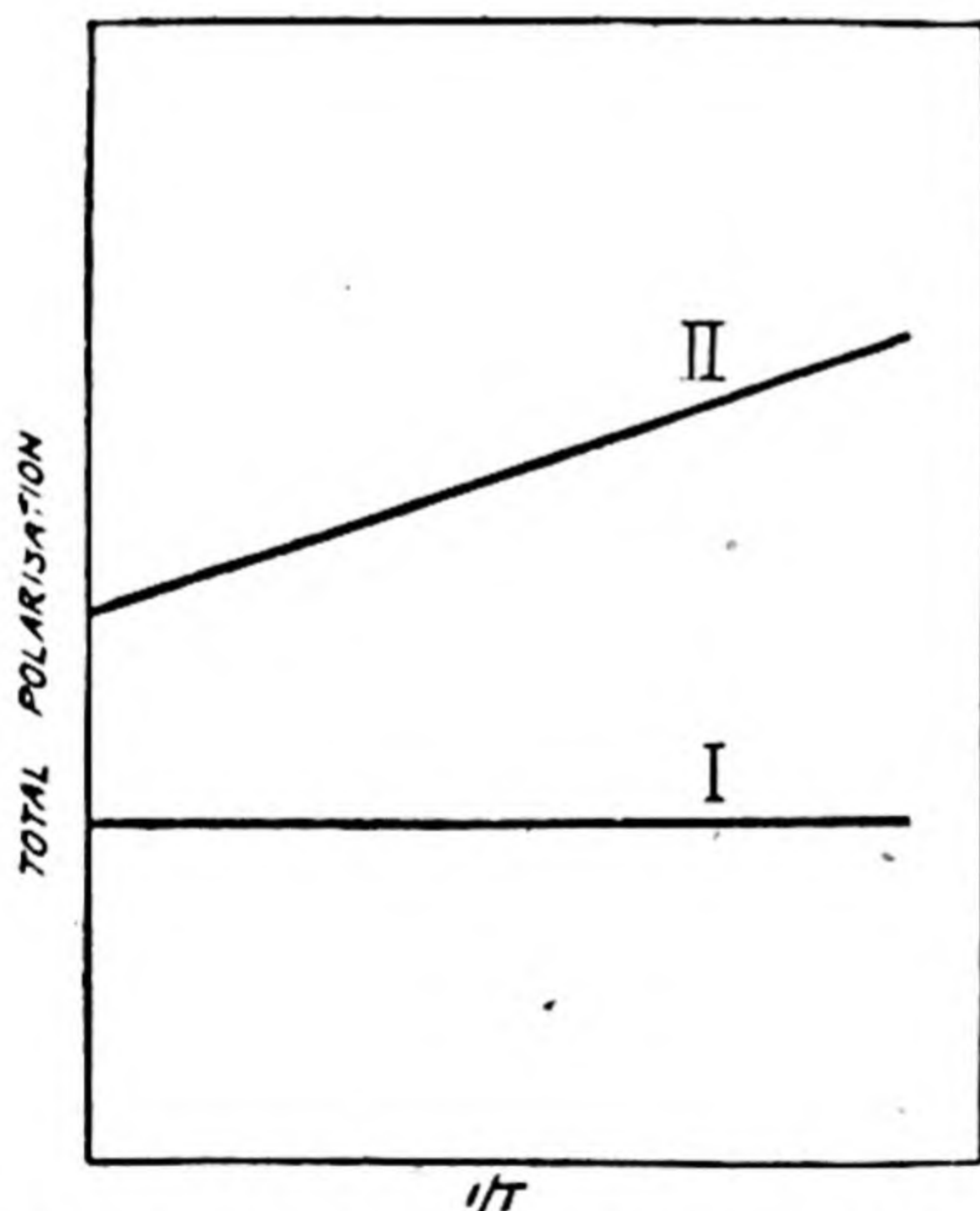


FIG. 4.—Variation of total polarisation with the reciprocal of the absolute temperature. Non-polar substances give curves of type I ; substances containing a permanent dipole give type II.

with  $b$  in c.c. According to equation (xix.), therefore, if the total polarisation, determined from the dielectric constant, is plotted against the reciprocal of the absolute temperature, the graph should be a straight line. For a non-polar molecule  $\mu$  is zero, and hence so also is  $b$ , and the plot of  $P$  against  $1/T$  should be a line parallel to the  $1/T$  axis (Fig. 4, I.); for a molecule with a permanent dipole, however, the plot should still be a straight line (Fig. 4, II.), but its slope  $b$  is directly related to the dipole moment



$\mu$ , by equation (xix.b). From measurements of dielectric constant and density of a gas at various temperatures it is thus possible to determine the permanent polar moment of the molecules. Incidentally the intercept  $a$  on the  $P$  axis gives the value of  $P_D$ , the total *distortion* polarisation.

This method has been used for many gases, and it has almost invariably been found that, in agreement with Debye's equation, a straight line is obtained on plotting  $P$  against  $1/T$ ; for polar molecules the value of  $\mu$  is determined from the slope of this line. For example, from the measurements of Jona (1919) on ammonia gas it can be shown that the slope ( $b$ ) of the  $P-1/T$  line is 15250 c.c.; hence

$$\begin{aligned}\mu_{\text{NH}_3} &= 0.0127 \times \sqrt{15250} \times 10^{-18} \text{ e.s.u.} \\ &= 1.57 \times 10^{-18} \text{ e.s.u.}\end{aligned}$$

All dipole moments are of the order of  $10^{-18}$  e.s.u.; this is in agreement with anticipation, since the unit electronic charge is  $4.77 \times 10^{-10}$  e.s.u., and molecular dimensions are of the order of  $10^{-8}$  cm., and so  $\mu$  must have a magnitude in the vicinity of  $10^{-18}$  e.s.u.\*

**The Refraction Method.** Since the accurate measurement of the variation of the dielectric constant of a vapour with temperature is not a simple matter an alternative method has been suggested for the determination of  $\mu$ ; it can, however, at best only be regarded as an approximate method. The Debye equation (xv.) may be written in the form

$$P = P_D + \frac{4\pi N}{3} \cdot \frac{\mu^2}{3kT} \quad \dots \quad \text{(xxi.)}$$

$$\therefore \mu = 0.0127 \times 10^{-18} \sqrt{(P - P_D)T} \quad \dots \quad \text{(xxii.)}$$

where  $P$  is the total, and  $P_D = (P_A + P_E)$  the deformation, polarisation;  $P_\mu$  is, of course, equal to  $P - P_D$ . The value of  $P_D$  could be determined from the Lorentz-Lorenz equation if the refractive index in the far infra-red were known, but as this is

\* Dipole moments are frequently expressed in terms of the "Debye" unit (symbol,  $D$ ), which represents a dipole moment of  $10^{-18}$  e.s.u. The moment for ammonia given above would then be 1.57  $D$ .



rarely available an approximation is obtained by using the refractive index for visible light. The molecular refraction is then really equal to  $P_E$ , but as  $P_A$  is generally small, the former may be regarded as almost equal to  $P_D$ ; the error involved in this assumption is naturally less marked if  $P_\mu (= P - P_D)$  is large. As an illustration of the method the following example may be cited: from the refractive index of ammonia gas the value of  $P_E$ , which is taken as equal to  $P_D$ , has been calculated as 5.7 c.c., whereas the total polarisation  $P$  evaluated from the dielectric constant at 19° C. is 57.6 c.c. Hence  $P - P_D$  is approximately 51.9 c.c., and the value of  $\mu$ , for  $T = 292^\circ \text{K.}$ , may be evaluated from equation (xxii.) as  $1.56 \times 10^{-18}$  e.s.u. This result is in good agreement with the one obtained by the accurate temperature method of Debye, and quoted in the previous paragraph. It must always be borne in mind that, since  $P_E$  is less than the whole of the distortion polarisation  $P_D$ , the value of  $P_\mu$ , and hence of  $\mu$ , calculated in this way is liable to be too large. When the use of this approximate method leads to small values of  $\mu$ , therefore, there is no certainty that the results have any significance; for example, naphthalene was found to have an apparent dipole moment of  $0.7 \times 10^{-18}$  e.s.u., whereas a zero value would have been expected on theoretical grounds. As a matter of fact more recent accurate work (Parts, 1930) has shown that naphthalene really has no permanent dipole moment.

Another method of determining  $P_D$  with greater accuracy is available if the substance can be easily obtained in the solid state, and its dielectric constant measured; it has already been stated that in this condition the value of  $P_\mu$  is zero, and so the measured value of the total polarisation is equal to  $P_D$ . For example,  $P$  for water vapour is 60.0 at 100° C., whereas  $P$  for ice is 9.5; hence  $P - P_D (= P_\mu)$  for water molecules is equal to 50.5. From this the dipole moment of water is calculated by means of equation (xxii.) as  $1.74 \times 10^{-18}$  e.s.u.; the accurate value determined from the variation of the dielectric constant of water vapour with temperature is  $1.85 \times 10^{-18}$  e.s.u. The reliability of this method depends on the assumption that no orientation of the molecular dipoles occurs when the solid is in an electrical field; it is not



certain that this assumption is always justifiable (Smyth and Hitchcock, 1932).

Wolf and his co-workers (1929 *et seq.*) have adopted a somewhat arbitrary means to allow for the  $P_A$  term; they suppose that this is always 15 per cent. of the electron polarisation  $P_E$ , determined from refractive index measurements. It is probable that in most instances this estimate of  $P_A$  is excessive. Until quite recently it was thought that the atom polarisation for some molecules was quite large, but it is now generally accepted (Smyth, 1933; Sugden, 1934) that  $P_A$  is usually less than 5 c.c. and rarely more than 10 c.c. Under these circumstances Sugden is of the opinion that an allowance of 5 per cent. of the electron polarisation, determined from the refractive index of the Na-D line, is quite adequate for the atom polarisation (see Groves and Sugden, 1935).

**The Molecular Beam Method.** The principle of the method used by Stern and his collaborators to determine the magnetic moments of atoms by studying their deviation in a non-homogeneous magnetic field has been extended to the measurement of dipole moments. The substance is placed in a minute oven and heated in an evacuated apparatus, at a temperature of about  $200^\circ$ ; the vaporised molecules are allowed to pass through two slits (1 mm.  $\times$  0.01 mm., and 2 mm.  $\times$  0.02 mm.) placed about 6 cm. apart. In this way a thin "molecular beam," in which the molecules are too far apart to collide, is picked out. At the end of the apparatus the beam strikes a metal plate cooled in liquid air, and there the molecules condense; the trace left as a result can be observed in a microscope, and any deviation, resulting from the application of an electric field, can be studied. In the absence of such a field the molecules move in a straight line through the slits, but when a non-homogeneous electric field is applied a deviation results. If the molecules are non-polar they acquire an induced moment in the field and the trace they leave is shifted laterally, but if polar molecules are present there is in addition a broadening of the trace. The extent of the broadening depends on the experimental conditions—strength and non-homogeneity of the electric field, dimensions of the beam, temperature, etc.—and on the dipole moment of the polar molecule. Working under constant condi-



tions the broadening of the beam may be taken as being proportional to the dipole moment, complications due to molecular rotation being ignored. By comparing the broadening obtained for any substance with that observed for a compound of known dipole moment the moment of the former may be calculated. The experimental difficulties in the method are very considerable and hitherto only approximate results have been obtained, but it has possibilities for substances which are not sufficiently volatile for their dielectric constants to be measured or which are not appreciably soluble in non-polar solvents. The method was first used to determine the dipole moment of salts (Wrede, 1927 ; Scheffers, 1934), which generally cannot be studied in any other way. It has been employed by Estermann and Wohlwill (1929, 1933) to investigate the dipole moments of pentaerythritol derivatives.

**Measurements in Dilute Solutions.** The first two methods described for determining the dipole moment of a molecule may be extended to dilute solutions ; this is a matter of great convenience, as for many substances measurement of the dielectric constant of the vapour is difficult to carry out experimentally. If the polar substance is dissolved in a non-polar solvent the tendency for dipole interaction to occur is relatively small, as a general rule, so that the total polarisation of the dilute solution may be regarded as being equal to the sum of the polarisations of the constituents. On the basis of this assumption the Debye equation becomes

$$P_{1,2} = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{f_1 M_1 + f_2 M_2}{d} = f_1 P_1 + f_2 P_2 \quad \dots \quad (\text{xxiii.})$$

where  $P_{1,2}$  is the total polarisation of a mixture of a non-polar substance 1, with a polar compound 2. The dielectric constant of the mixture is  $\epsilon$ , and  $d$  is its density, whereas  $f$ ,  $M$  and  $P$  refer to the molar fraction, molecular weight and total polarisation, respectively, of the two species designated by the suffixes 1 and 2. From the known composition of various mixtures and the measured dielectric constant it is thus possible to calculate  $P_1$  and  $P_2$ . Alternatively, since the substance 1 is non-polar, the value of  $P_1$



may be determined by direct measurement of its dielectric constant in the pure liquid, and so  $P_2$  evaluated for each mixture. The calculations may be considerably simplified by rearranging equation (xxiii.) so that it may be expressed in the form (Sugden, 1934 ; de Bruyne, 1934) :

$$P_2 = M_2 \left( p_1 + \frac{p_{1,2} - p_1}{w_2} \right) \quad . \quad . \quad . \quad . \quad (\text{xxiv.})$$

where the  $p$  terms are the specific polarisations, defined by the equation

$$p = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{1}{d} \cdot \dots \quad (\text{xxv.})$$

and  $w_2$  is the *weight* fraction of solute in the given solution.

The results in Table XXX. are for a series of mixtures of *cyclohexane* and *chloroform*; of these substances the former has no permanent dipole whereas the latter has, and so they are designated by the suffixes 1 and 2, respectively, in equations (xxiii.) and (xxiv.).

TABLE XXX.—*Polarisations of Cyclohexane-Chloroform Mixtures*

<i>Cyclohexane</i> <i>f</i> <sub>1</sub> .	<i>Chloroform</i> <i>f</i> <sub>1</sub> .	<i>d</i> 20°.	<i>ε</i> 20°.	<i>P</i> <sub>r</sub> .
1.0000	0.0000	0.7784	2.032	—
0.9187	0.0813	0.8208	2.163	51.36
0.8164	0.1836	0.8770	2.324	49.14
0.4315	0.5685	1.1285	3.270	47.36
0.2148	0.7852	1.2960	3.959	46.50
0.0000	1.000	1.4890	4.816	44.89

The total polarisation  $P_2$  of the chloroform is seen to vary somewhat with concentration of the solution; this type of behaviour is relatively common, and suggestions have been made to allow for it by including a correction term in the Debye equation. Hedestrand (1929) and van Arkel and Snoek (1934) have proposed equations by which the polarisation of the solute may be extrapolated to infinite dilution, and from this the dipole moment is



evaluated. For most purposes it is sufficient to extrapolate the  $P_2$  values graphically, for in any case the results obtained are to some extent approximate, as will be seen subsequently. The falling off in the polarisation of the solute with increasing concentration is often due to dipole association, but the main factor responsible is the change in the dielectric constant of the medium and this aspect of the question will be taken up later in connection with the general problem of solvent influences.

Having obtained the total polarisation for the polar substance, one of the methods used for gases may be applied in order to determine the orientation polarisation  $P_\mu$ ; in the first place  $P_2$  may be determined for different temperatures and the slope  $b$  of the  $P_2 - 1/T$  curve measured, and so  $\mu$  calculated as described for gases. This method is very sensitive to errors, and since the  $P_2$  values for infinite dilution are not always accurate the results are often unsatisfactory; the procedure is, therefore, rarely employed. Alternatively,  $P_E$  may be evaluated from the refractive index for the sodium-D line of the pure solute, or of suitable solutions, by means of equation (xvii.), and this may be assumed to be equal to  $P_D$ , or a small allowance can be made for the atom polarisation (p. 141); the dipole moment can then be calculated with the aid of equation (xxii.). From Table XXX. it is seen that at  $20^\circ$  the total polarisation of chloroform at infinite dilution is about 52; the refractive index for the sodium-D line at  $20^\circ$  is 1.4462 and the density 1.4890, and so  $P_E$  is 21.40. If an allowance of 5 per cent. is made for  $P_A$ , it follows that  $P_\mu$  is equal to 29.5 c.c., and hence the dipole moment is  $1.18 \times 10^{-18}$  e.s.u., by equation (xxii.).

**Influence of Solvent.** Until 1932 it was generally believed that, provided there was no compound formation, nor any change in the positions of the electrons or in the configuration of the solute under examination, the solvent had no influence on the polarisation provided the results were extrapolated to infinite dilution. In that year Müller published accurate measurements for chlorobenzene in a number of solvents, and these have been followed by data for other solutes, which show beyond doubt that the solvent does have an appreciable effect. Some of the polarisation



values obtained for chlorobenzene and for methylene chloride are quoted in Table XXXI.

TABLE XXXI.—*Influence of Solvent on Polarisation of Chlorobenzene and Methylene Chloride*

Solvent.		Polarisation at 20°.	
		Chlorobenzene.	Methylene Chloride.
Carbon disulphide .	2.64	75.5	62
Benzene . . . .	2.28	81	68
Carbon tetrachloride .	2.23	81	70
Decalin . . . .	2.16	83	69
Cyclohexane . . .	2.02	84	—
Hexane . . . .	1.91	86	71.5

It is seen from the results that as the dielectric constant of the solvent is decreased the polarisation of the solute increases: this implies that the effect is due to some kind of electrical interaction and that the correct value would be obtained by extrapolation to  $\epsilon = 1$ , which would correspond to a vacuum. Müller proposed the empirical formula

$$\frac{P_{\mu}(\text{solution})}{P_{\mu}(\text{vacuum})} = 1 - k(\epsilon - 1)^2 \quad . \quad . \quad . \quad (\text{xxvi.})$$

where  $k$  is constant for all substances, and is equal to  $0.075 \pm 0.005$ . This relationship is not satisfactory in all cases, but it is sufficient to show that the value of  $P_{\mu}$  in a solvent having a dielectric constant of about 2 should be about 7 per cent. lower than the true value.

Another equation which is applicable in many instances is that suggested by Sugden (1934), thus

$$P_2 = A - B \frac{\epsilon - 1}{\epsilon + 2} \quad . \quad . \quad . \quad . \quad (\text{xxvii.})$$

where  $P_2$  is the total polarisation of the solute in the solution of dielectric constant  $\epsilon$ , and  $A$  and  $B$  are constants. The quantity



$(\epsilon - 1)/(\epsilon + 2)$  is known as the volume polarisation, and is the polarisation per cubic centimetre of the solution: hence it is suggested that the measured molar polarisation of the solute is a linear function of the volume polarisation of the solution. The relationship of equation (xxvii.) should be applicable not only to the influence of different solvents on the measured polarisation of a solute, but it should account for the variation of  $P_2$  with concentration, as shown in Table XXX. From a study of various data it has been suggested (Sugden, 1934) that the constant  $A$  is equal to the correct value of  $P_2$ , as obtained from measurements on the vapour, plus a small constant, whereas  $B$  is the true orientation polarisation  $P_\mu$ , from which the dipole moment is determined. This interpretation of equation (xxvii.) should provide a method for extrapolating  $P_2$  simultaneously to zero concentration and unit dielectric constant; the values of the measured polarisation at various concentrations in a given solvent are plotted against the corresponding volume polarisation, and the slope of the straight line gives  $P_\mu$ . By adopting this procedure Fairbrother (1934) has obtained the dipole moment of nitrobenzene as  $4.24D$ , which is almost identical with the  $4.28D$  found by Groves and Sugden (1934) by the temperature method with the vapour. It is quite possible, however, that this agreement is fortuitous, since the equation (xxvii.) is by no means rigidly obeyed by nitrobenzene solutions (Jenkins and Sutton, 1935), and is certainly not universally applicable.

Goss (1934) has shown that the equation of Raman and Krishnan (1928), which corrects the Debye equation (xv.) for the optical and electrical anisotropy of the molecules, can be reduced to a form similar to Sugden's relationship considered above for the solvent effect; the significance of the constants  $A$  and  $B$  is, however, different. The former is now shown to represent the vapour value for  $P_2$ , without the small constant found by Sugden, but  $B$  instead of being equal to the orientation polarisation is a term which includes factors for the effect of the anisotropy of the medium, that is the different polarisability in different directions, on the electron and orientation polarisations. For the evaluation of dipole moments the measured values of  $P_2$  at infinite dilution



in different solvents, and for the pure liquid, are plotted against  $(\epsilon - 1)/(\epsilon + 2)$ ; the straight line is extrapolated to  $\epsilon = 1$ , so as to give the ideal value of  $P_2$  from which the dipole moment may be calculated, after allowing for the distortion polarisation. In the form used by Goss, equation (xxvii.) has an important consequence: both the Müller and the Sugden relationships require that the polarisation in solution should be *less* than in the vapour phase, but according to the theoretical deductions of Raman and Krishnan the factor  $B$  may have negative values for certain substances, so that there is a possibility of the measured dipole moment in solution being greater than the true value (Le Fèvre, 1935). This appears to be the case for chloroform, and possibly for ether and other substances.

An important contribution to the subject under discussion has been made by Frank (1985) who, following Weigle (1983), has attempted a theoretical treatment of the solvent effect. This is based on the argument that when a polar molecule is placed in a polarisable medium it sets up induced dipoles in the surrounding solvent molecules; there is, in general, a resultant moment due to the latter which must be combined vectorially (*vide infra*) with the primary moment, and is in fact an essential part of the total moment in solution. In the vapour phase, of course, this additional moment is absent. The net moment induced in the solvent molecules will depend not only, as is to be expected, on the primary dipole moment and on the dielectric constant of the medium, but also on the shape of, and the positions of the individual moments in, the solute molecule. This dependence of the solvent effect on the geometry and nature of the molecules of dissolved substance had been realised by Higasi (1984); by Müller and Mortier (1985), and by Le Fèvre (1985, 1986); the connection between polarisation and electrical anisotropy deduced by Raman and Krishnan (1928) implies a relationship of an analogous type. The equation deduced by Frank takes the form

$$\frac{\Delta\mu}{\mu} = A \frac{\epsilon - 1}{\epsilon} . . . . . (\text{xxviii.})$$

where  $\mu$  is the true dipole moment of the solute, and  $\Delta\mu$  is the



change resulting from measurement in a solvent of dielectric constant  $\epsilon$ . The constant  $A$  depends on the configuration of the molecule and can be evaluated graphically. For molecules which are virtually symmetrical  $A$  is positive, so that the dipole moment is greater in solution than in the vapour; this is supposed to be the case for the hydrogen halides. Fairbrother (1932-34) had found differences of this type, and had attributed them to an electronic displacement in the molecule, of the nature of incipient ionisation, brought about by the solvent, but Frank is of the opinion that they follow from a normal solvent effect. Molecules such as methyl chloride, chlorobenzene and nitrobenzene, with a radical on the dipole axis should have negative values of  $A$ , but for substances with a single radical not on the dipole axis, *e.g.*, alcohols, or with radicals off the dipole axis but with axial symmetry, *e.g.*, symmetrical ethers and ketones, the solvent effect can be positive, negative or zero, according to the configuration of the molecule. As a general rule a large valency angle in ethers, ketones or amines should result in the dipole moment being greater in solution than in the vapour. Although the theoretical treatment appears promising, it is doubtful if it is sufficiently developed to be of any direct quantitative value, for it appears that equation (xxviii.) is not sufficiently accurately obeyed for a given solute in a number of different solvents for it to be of use in extrapolating measured polarisations to a dielectric constant of unity.

It must be concluded, therefore, that no reliable method is yet available for correcting polarisations or dipole moments measured in solution for the effect of the solvent: it is evident, however, that a medium of low dielectric constant should be used if possible. Where the change of polarisation with concentration is considerable, as is generally the case with solutes of high dipole moment, measurements should be made in very dilute solutions, so that the extrapolation to zero concentration is reasonably accurate. For compounds of relatively small moment the solvent error is not considerable; and neither, as a rule, is the variation of polarisation with concentration. A few results, to show the differences between the true dipole moments, as determined from the vapour, and the



values in solution, generally benzene, are given in Table XXXII. ; they illustrate the different types of behaviour.

TABLE XXXII.—*Dipole Moments from Measurements with Vapour and Dilute Solutions*

Substance.	Dipole Moment in Debye Units.	
	Vapour.	Solution.
Chloroform . . . . .	1.05.	1.15
Ether . . . . .	1.14	1.2
Methyl alcohol . . . . .	1.68	1.65
Chlorobenzene . . . . .	1.73	1.6
Water . . . . .	1.84	1.9
Acetophenone . . . . .	3.00	2.90
Nitrobenzene . . . . .	4.23	4.00

**Results of Measurements.** Since 1924 a very large number of studies has been made of the dipole moments of molecules of various kinds, and the results have been used, apart from their own intrinsic interest, to throw light on problems of chemical constitution. Before proceeding to discuss some instances of this application a short résumé will be given in Table XXXIII. of the general results obtained in the measurement of the permanent polar moments of various types of compounds. Full lists of data may be found in the monograph by Smyth (1931), in the article by Wolf and Fuchs in Freudenberg's "Stereochemie" (1932), and especially at the end of the report of the Faraday Society Discussion on "Dipole Moments," 1934.

## INORGANIC COMPOUNDS

**The Structure of the Simple Molecules.** A study of the values of the dipole moments quoted in Table XXXIII. leads to a number of interesting conclusions concerning molecular structure, and allied subjects ; some of the results will now be considered. In the first place inorganic compounds will be discussed. The



TABLE XXXIII

*Dipole Moments of Molecules in Debye Units*

<i>Inorganic Compounds</i>			
Hydrogen . . . . .	0	Phosphine . . . . .	0.55
Nitrogen . . . . .	0	Arsine . . . . .	0.16
Nitrous oxide . . . . .	0.14	Water . . . . .	1.84
Carbon dioxide . . . . .	0	Hydrogen sulphide . . . . .	1.10
Carbon disulphide . . . . .	0	Hydrogen cyanide . . . . .	2.6
Hydrogen chloride . . . . .	1.03	Carbon monoxide . . . . .	0.12
Hydrogen bromide . . . . .	0.78	Sulphur dioxide . . . . .	1.6
Hydrogen iodide . . . . .	0.38	Iodine . . . . .	0
Hydrogen peroxide . . . . .	2.1	Bromine . . . . .	0
Ammonia . . . . .	1.49	Chlorine . . . . .	0
Silver perchlorate . . . . .	4.7		
Phosphorus tri- chloride . . . . .	0.9		
Arsenic trichloride . . . . .	2.15		
Antimony tri- chloride . . . . .	3.75		
Stannic iodide . . . . .	0		
Stannic chloride . . . . .	0		
Boron trichloride . . . . .	0		
Hydrazine . . . . .	1.84		
<i>Organic Compounds : Aliphatic</i>			
Paraffins . . . . .	0	Alkyl chlorides . . . . .	2.05
Carbon tetra- chloride . . . . .	0	Alkyl bromides . . . . .	2.05
Olefines . . . . .	0.5 ?	Alkyl iodides . . . . .	1.9
Acetylene . . . . .	0	Dichloromethane . . . . .	1.5
$\alpha$ -Butylene . . . . .	0.37	Chloroform . . . . .	1.15
Ethers . . . . .	1.15	Alcohols . . . . .	1.7
Sulphides . . . . .	1.55	Mercaptans . . . . .	1.35
Methyl chloride . . . . .	1.86	Ketones . . . . .	2.8
Methyl bromide . . . . .	1.80	Acetaldehyde . . . . .	2.7
Methyl iodide . . . . .	1.35	Butyraldehyde . . . . .	2.46
		Esters . . . . .	1.8
Nitriles . . . . .	3.6		
Primary amines . . . . .	1.3		
Secondary amines . . . . .	1.0		
Tertiary amines . . . . .	0.76		
Nitromethane . . . . .	3.42		
Acetic acid . . . . .	1.4		
Butyric acid . . . . .	1.4		
Ethylene oxide . . . . .	1.88		
Cyclohexane . . . . .	0		
Methyl cyclohexane . . . . .	0		
Cyclohexanone . . . . .	2.7		
<i>Aromatic</i>			
Benzene . . . . .	0	Benzaldehyde . . . . .	2.75
Naphthalene . . . . .	0	Benzoic acid . . . . .	0.8
Diphenyl . . . . .	0	Methyl benzoate . . . . .	1.8
Toluene . . . . .	0.4	Fluorobenzene . . . . .	1.57
Phenol . . . . .	1.70	Chlorobenzene . . . . .	1.73
Anisole . . . . .	1.2	Bromobenzene . . . . .	1.71
Quinoline . . . . .	2.18	Iodobenzene . . . . .	1.2
Diphenyl ether . . . . .	1.15	Benzophenone . . . . .	2.95
Acetophenone . . . . .	3.00		
Dibenzylketone . . . . .	2.65		
Benzonitrile . . . . .	4.87		
Aniline . . . . .	1.56		
Diphenylamine . . . . .	1.3		
Dimethylaniline . . . . .	1.2		
Nitrobenzene . . . . .	4.23		
Benzoic esters . . . . .	1.9		

For other results see Tables XXXV.—XXXVII., and pp. 156, 159.

absence of any permanent polarity in argon, hydrogen and nitrogen is not surprising, since such molecules are quite symmetrical and no displacement of the electrical charges would be expected in the normal molecule. With carbon dioxide, and the closely related carbon disulphide and nitrous oxide, the absence of a permanent dipole has an important implication. There are two obviously reasonable structures possible for carbon dioxide; these are



represented in Fig. 5, *A* and *B*. In the structure *A* the C — O valency linkages make an angle with one another, but in the *B* alternative the molecule as a whole is linear. It is well known that the oxygen atom tends to become negatively charged, and so the carbon dioxide molecule presumably contains two permanent dipoles, the directions of which are along the linkages.

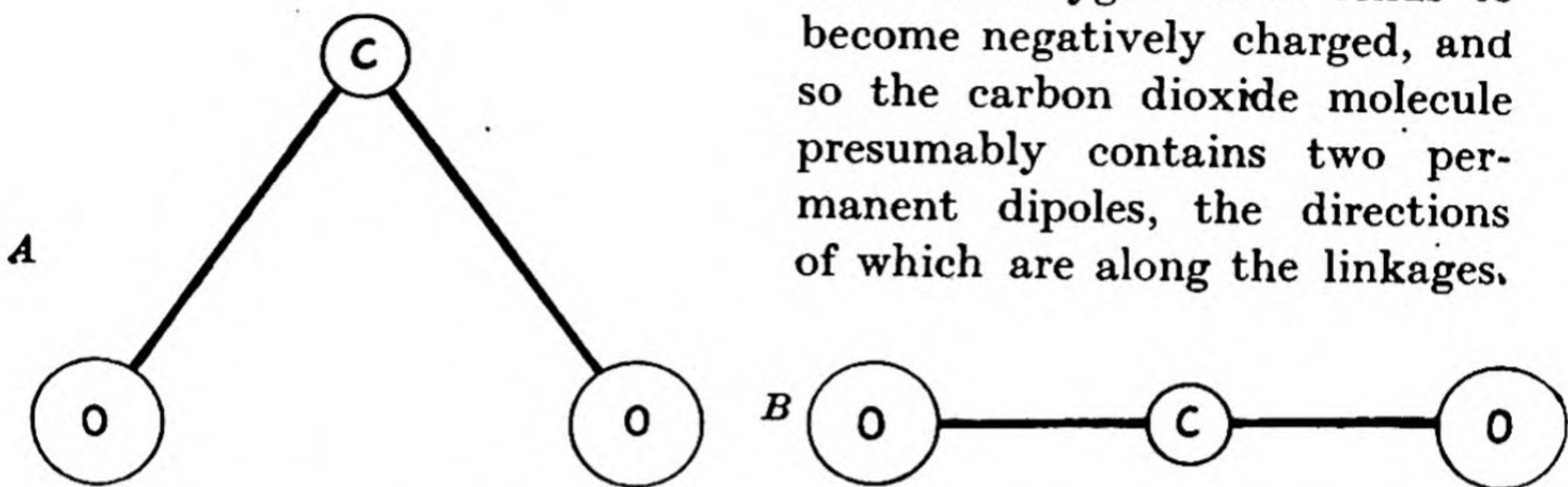


FIG. 5.—Two possible structures for the carbon dioxide molecule ; formula *A* should have a net dipole moment, but the moment of *B* would be zero.

The fact that the resultant dipole moment determined experimentally is zero indicates quite definitely that the *A* formula is not correct, for such a model would undoubtedly have a resultant moment. In the *B* formula, however, the two moments, which must be exactly equal, act in diametrically opposite directions, so that the net dipole moment for the molecule should be zero. It is clear, therefore, that carbon dioxide, and presumably the disulphide, possess molecules of a linear type. Since nitrous oxide and carbon dioxide have so many physical properties in common (p. 19) it is probable that the former also has a linear molecule ; the significance of the small dipole moment is, however, not immediately evident since the atomic arrangement is in any case unsymmetrical, viz., NNO. The observed value is in harmony with the view (Pauling, 1932) that in nitrous oxide resonance occurs between the two states  $\bar{\text{N}}=\text{N}^+=\text{O}$  and  $\text{N}\equiv\text{N}^+-\bar{\text{O}}$ , both of which are linear ; the large moments due to the semi-polar bonds act in opposite directions and so tend to cancel in the actual molecular configuration.

**The Water Molecule.** Since water has a fairly large permanent dipole moment, it cannot form a symmetrical linear molecule ;



a disymmetrical molecule of the type shown in Fig. 6 would account for the dipole, but such a structure has been shown to be mechanically unstable. The only conclusion to be drawn from the results is that a triangular model is applicable to water,



FIG. 6.—A possible disymmetrical structure for the water molecule; this structure is, however, dynamically unstable.

the two valencies of the oxygen atom being inclined at an angle. Debye (1929) has examined the values for the moments of inertia of the water molecule as determined from measurements of its infra-red spectrum (see Chapter IV.); the data are in agreement with two possible structures for the water molecule (Fig. 7). The first of these, Fig. 7, *A*, involves an angle  $\theta$  of  $64^\circ$  between

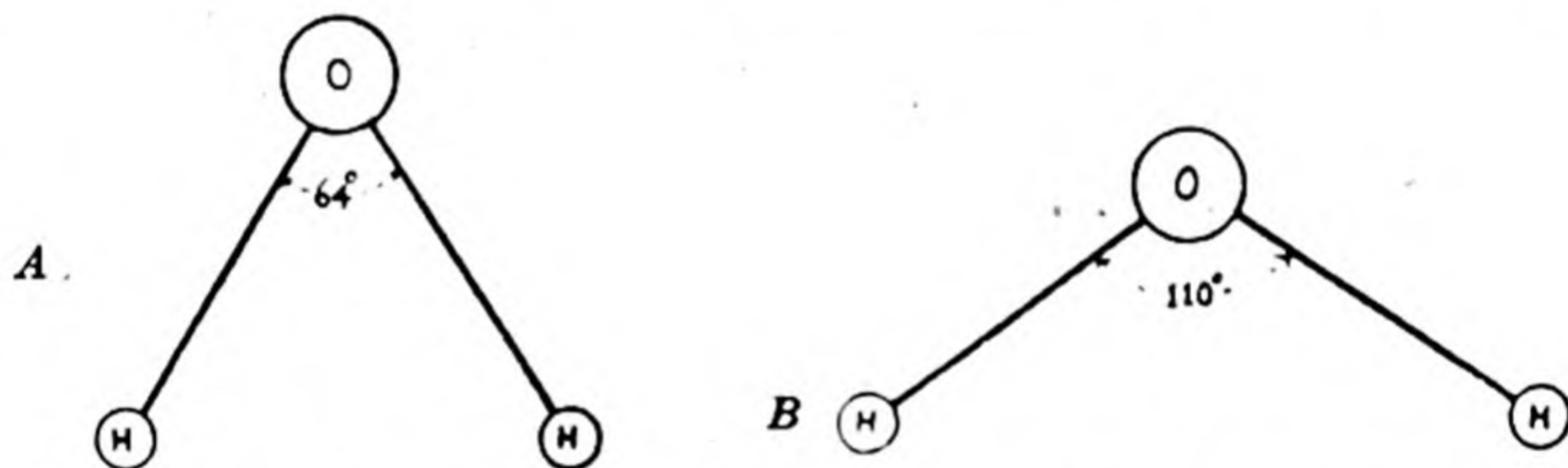


FIG. 7.—Two possible symmetrical structures for the water molecule, based on known values of the moments of inertia; the angle  $\theta$  between the H—O linkages is  $64^\circ$  in formula *A*, and  $110^\circ$  in formula *B*. (After Debye.)

the two H—O linkages, whereas the second, *B*, requires an angle  $\theta$  of  $110^\circ$ , taking the known values for the dimensions of the hydrogen and oxygen atoms. It is obvious that these two models will correspond to very different dipole moments, and the values calculated are  $1.34 \times 10^{-18}$  for model *A*, and  $4.34 \times 10^{-18}$  e.s.u. for model *B*; the actual value is about  $1.8 \times 10^{-18}$ . The fair agreement with the result for formula *A* led Debye to suggest that the oxygen valency angle was about  $64^\circ$ , but it is now known that the calculation was incorrect, because of the failure to take



into account the deformation of the electronic system of the oxygen atom. This effect is very marked in the hydrogen halides (*vide infra*). Further investigation of the spectrum of water vapour has shown that the angle  $\theta$  is about  $106^\circ$ , which is somewhat larger than the value deduced by wave-mechanical methods (p. 70).

**The Ammonia Molecule.** From Table XXXIII. it may be seen that ammonia has also a large permanent moment; if the three hydrogen atoms and the nitrogen were in the same plane and the former arranged symmetrically about the latter there would be no moment, and even if the arrangement were not quite symmetrical, the moment would be very small. The existence of a definite dipole moment indicates that the nitrogen atom is not in the plane containing the three hydrogen atoms; this conclusion is in harmony with the theory proposed several years ago by Hantzsch and Werner in order to account for the stereochemistry of nitrogen compounds. The result is also in accord with that obtained from a study of the infra-red spectrum of ammonia gas, from which it appears that the molecule is tetrahedral with the three hydrogen atoms in one plane, and the nitrogen atom at the apex. It is not implied, by any means, that the tetrahedron is a regular one, for the height of the nitrogen atom above the plane of the hydrogen atoms is very much less than a regular tetrahedron would require. The results for phosphine and arsine indicate that these molecules have structures similar to that of ammonia; the large diminution in the value of the dipole moment as the size of the negative atom increases is due partly to the fact that the height of the tetrahedron becomes less—this is borne out by the infra-red spectra—and partly to the distortion of the electron centre of gravity of the large atom towards the electrical centres of the positive hydrogen atoms.

**Distortion of Electronic Fields.** Since the distances apart of the two nuclei,  $d$ , in the hydrogen halides are known from infra-red measurements it should be possible to calculate the dipole moments on the assumption that the electrical centres and the mass centres coincide. Strictly speaking this would only be true if the molecule consisted of two ions. Taking the charge to be equal to that of the



electron ( $4.77 \times 10^{-10}$  e.s.u.), the calculated values for  $\mu$ , together with the observed values, are given in Table XXXIV.

The striking differences between the observed and calculated dipole moments, which increase so markedly with increasing size of the halogen atom, can only be due to the deformation of the electron system of the latter by the hydrogen atom. The separa-

TABLE XXXIV

*Observed and Calculated Dipole Moments of Hydrogen Halides*

Substance.	$d$ (cm.)	$\mu$ (cal.).	$\mu$ (obs.).
Hydrogen chloride .	$1.28 \times 10^{-8}$	$6.1 \times 10^{-18}$	$1.03 \times 10^{-18}$
Hydrogen bromide .	1.42	6.8	0.79
Hydrogen iodide .	1.62	7.6	0.36

tion of the electrical centres is much less than the distance between the centres of gravity of the nuclei, and the difference between these two quantities increases with the atomic weight of the halogen atom. The distortion of the electron system from the ideal ionic state is much more marked for the iodine atom than for the bromine, and still more than for the chlorine atom. These conclusions are in agreement with the views on the tendency to share electrons rather than to form a polar linkage, put forward by Fajans as a result of his work on refraction (p. 21).

**Dipole Moments of Salts.** Although a simple, unsolvated ion probably cannot be considered to have a permanent moment the undissociated molecule of a salt, and probably a solvated ion, should have a considerable dipole moment, but it is difficult to test this point experimentally. Unfortunately salts are almost invariably insoluble in non-polar solvents, and solutions in this type of solvent are essential for determining the moment of such solutes. By the use of the molecular beam method (p. 141), however, the dipole moments of potassium, thallous and sodium iodides, caesium chloride and rubidium bromide vapours have been determined (Wrede, 1927; Scheffers, 1935); the



values were all found, in agreement with anticipation, to be in the vicinity of  $10 \times 10^{-18}$  e.s.u. Owing to the difficulties of the method the results are only very approximate.

Silver perchlorate is exceptional as being an inorganic salt soluble in benzene; the dipole moment of this compound (Williams and Allgeier, 1927) and of a number of quaternary ammonium salts have been measured in benzene solution (Kraus, 1934, 1936). The moments all lie between 7 and  $20 \times 10^{-18}$  e.s.u. It will be noted that stannic chloride and iodide have zero moments, but this fact unfortunately throws no light on the polar nature of the linkages in the molecule. It is most probable that the four halogen atoms are arranged at the corners of a tetrahedron, with the tin atom at the centre, so that however large the Sn — Hal dipole might be, the four moments would cancel one another exactly. The comparatively large dipole moment of antimony trichloride as compared with those for phosphorus and arsenic trichloride, all of which probably have configurations similar to that of ammonia, indicates a tendency towards ionisation; this is in agreement with the position of antimony in the periodic classification.

## ORGANIC COMPOUNDS

**Moments in a Homologous Series.** In Table XXXIII. of dipole moments of organic compounds it will be observed that in several instances an individual substance is not mentioned, but only a group of substances, *e.g.*, alcohols, nitriles, etc. This is meant to imply that the dipole moment is almost independent of the residue attached to the — OH group in an alcohol, or to the — CN group in a nitrile, for example, provided of course that the residue does not contain another polar group. Strictly speaking this is, in general, only true for members of a homologous series beyond the second or third; the moments of the first two members are generally lower. The results given in Table XXXV. are taken from the compilations of Smith (1933) and of Cowley and Partington (1935); they show the effect of ascending a homologous series of straight-chain aliphatic compounds in a number of instances.

406. 370



TABLE XXXV.—*Dipole Moments in Homologous Series*  
(Debye Units)

Alkyl Group.	Chloride.	Bromide.	Nitrile.	Alcohol.	Amine.
Methyl . . .	1.86	1.78	3.44	1.65	1.23
Ethyl . . .	2.04	2.02	3.57	1.70	1.3
<i>n</i> -Propyl . . .	2.04	—	3.57	1.66	1.4
<i>n</i> -Butyl . . .	2.04	1.97	3.57	1.65	1.3

The increase of moment generally observed in passing from the methyl to the ethyl derivative has been attributed to the fact that the dipole of the polar group induces a moment in the hydrocarbon chain which acts in the same direction as the primary moment. It might be expected that this induction will be relayed down the hydrocarbon chain of the alkyl group as its length is increased, but the results show that the effect dies out very rapidly after the second carbon atom. For the alcohols and amines the induced moments are evidently very small: the explanation of this fact is that the effective moments of the —OH and —NH<sub>2</sub> groups act in directions which make an angle to the line of the hydrocarbon chain (*vide infra*). The component of the induced moment in the direction of the primary moment is consequently very small, and hence has little influence on the latter. The striking constancy in the dipole moment of the members of a homologous series, beyond the second, implies that the property is not primarily a function of the molecule but of the polar group, or more correctly of the polar linkages, as will be seen later.

### ADDITIVITY OF DIPOLE MOMENTS

**Group Moments.** As a corollary to the statement that the dipole moment of a molecule depends on the polar group, it is not improbable to suppose, as Sir J. J. Thomson suggested (1923), that the moment of a molecule containing several polar groups is the sum of the values for the constituent groups. Since



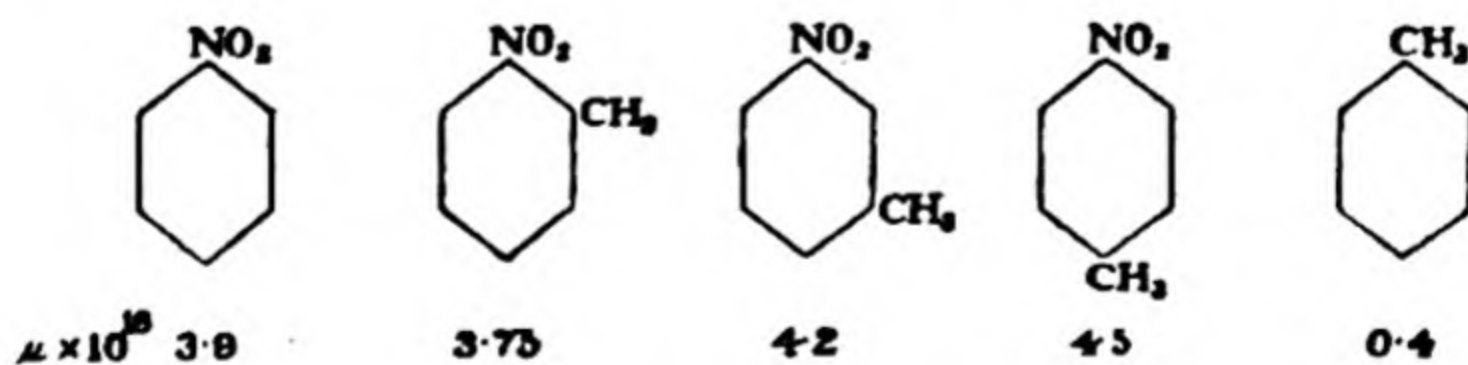
the dipole moment is a directional quantity it is of course necessary to sum the terms vectorially, as in the parallelogram of forces. From the dipole moments of various benzene substitution compounds Williams (1928) has derived the moments contributed by a number of groups on the assumption that the benzene ring residue is itself non-polar ; these values are given in Table XXXVI., in which are also included the moments for the — CN and — I radicals, when attached to a benzene ring. The data are taken from measurements in solution, and so cannot be regarded as correct ; they are satisfactory for present purposes, since they will be used in conjunction with other results obtained under similar conditions.

TABLE XXXVI

*Dipole Moments (e.s.u.  $\times 10^{-18}$ ) of Groups Attached to Benzene Ring*

NO <sub>2</sub>	CN	NC	CHO	OH	Cl	Br	I	COOH	H	CH <sub>3</sub>	NH <sub>2</sub>
— 3.9	— 3.8	— 3.6	— 2.8	— 1.7	— 1.5	— 1.5	— 1.25	— 0.9	0	+ 0.4	+ 1.5

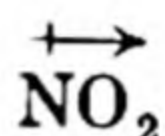
It will be noted that algebraic signs have been applied to the various figures ; these are determined as follows (Højendahl, 1926). Consider the measured dipole moments for the series of nitro-toluenes given below ; the values for nitrobenzene and for toluene are included.



It is clear that the moments of the two constituents, namely,  $3.9 \times 10^{-18}$  for the nitro-group and  $0.4 \times 10^{-18}$  for the methyl group, must operate in opposite directions from the nucleus in order to produce a resultant moment of  $4.5 \times 10^{-18}$  in the *p*- compound ; if the moments had the same sign, for example if both were directed towards the nucleus, the resultant would be equal approximately to the difference between 3.9 and 0.4, viz., 3.5, instead of  $4.5 \times 10^{-18}$  e.s.u. The nitro-group is known, from its

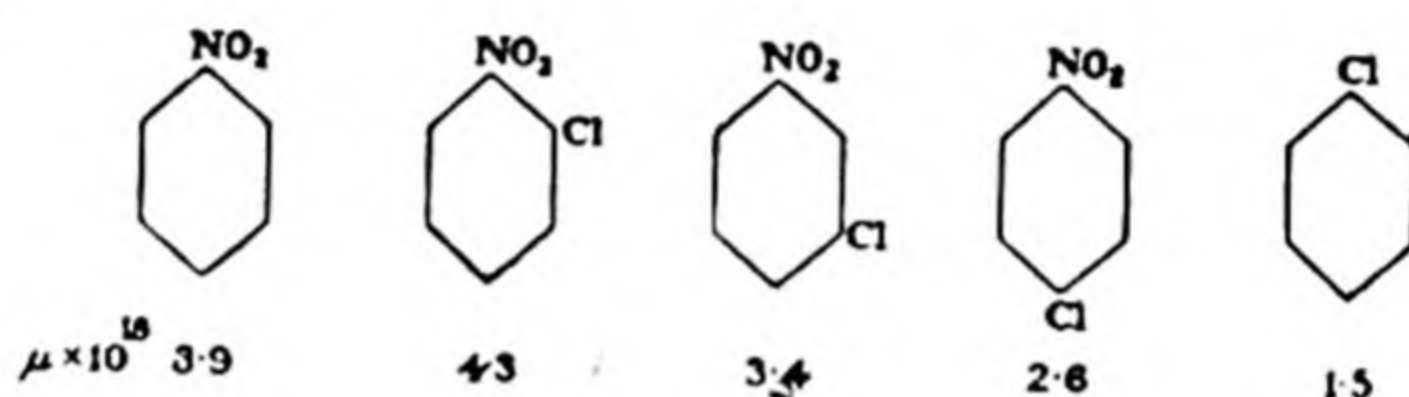


general chemical properties, to be a typical "negative," or electron attracting, radical, and so its dipole may be regarded as directed away from the benzene nucleus, and given a negative sign; the sign for the dipole of the  $\text{CH}_3$  group must, therefore, be regarded as positive (see Table XXXVI.). Sidgwick (1930) has suggested that the direction of the dipole be represented in the manner



which shows at once the positive end of the dipole and its direction.

The moments for the chloro-nitro-derivatives of benzene are as follows :



and hence it appears that the dipoles of both the nitro-group and the chlorine atom have the same sign. The value for the latter is, therefore, taken as  $-1.5D$ .

**Vector Addition of Dipole Moments.** In general if  $m_1$  and  $m_2$  represent the dipole moments, including the sign, of two groups substituted in a benzene ring, and  $\theta$  is the angle at which the directions of the moments are inclined, then the vector sum of the two dipoles, and hence the dipole moment of the compound, is given by

$$\mu = \sqrt{m_1^2 + m_2^2 + 2m_1m_2 \cos \theta} \quad . \quad . \quad (\text{xxix.})$$

If the benzene molecule is assumed to be flat, and there is much evidence in favour of this view, then the angle between the dipoles in an *o*-compound may be taken as  $60^\circ$ , and for *m*- and *p*- compounds as  $120^\circ$  and  $180^\circ$ , respectively. By means of equation (xxix.) it is thus possible to calculate the value of  $\mu$  for various di-substituted benzene derivatives, using the known figures (Table XXXVI.) for the contributions of the separate groups. Some results obtained in this way, together with the observed values, are given in Table XXXVII. (Smallwood and Herzfeld, 1930).



**Induced Dipoles and Distortion of Groups.** The agreement between the observed and calculated values is reasonably good, and lends support to the general theory of vector addition. Several authors have attributed the divergences to the fact that each group is subjected to an electric field, acting through space, due to the other polar groups; in each group, therefore, an induced dipole will be produced which will affect the total moment of the molecule. On the basis of this theory Smallwood and Herzfeld (1930) have applied corrections to the calculated values for  $\mu$  given in Table XXXVII.; the results obtained in this way

TABLE XXXVII

*Observed and Calculated Dipole Moments ( $\times 10^{18}$ ) of Substituted Benzene Derivatives*

Substance.	$m_1$ .	$m_2$ .	$\theta$ .	$\mu$ cal.	$\mu$ obs.
<i>o</i> -dichlorobenzene .	- 1.55	- 1.55	60°	2.68	2.25
<i>m</i> - " " .	"	"	120°	1.55	1.48
<i>p</i> - " " .	"	"	180°	0	0
<i>o</i> -dinitrobenzene .	- 3.90	- 3.90	60°	6.75	6.05
<i>m</i> - " " .	"	"	120°	3.90	3.81
<i>p</i> - " " .	"	"	180°	0	0
<i>o</i> -chloronitrobenzene .	- 1.55	- 3.90	60°	4.78	4.25
<i>m</i> - " " .	"	"	120°	3.26	3.38
<i>p</i> - " " .	"	"	180°	2.11	2.55
<i>o</i> -nitrotoluene .	- 3.90	+ 0.43	60°	3.70	3.75
<i>m</i> - " " .	"	"	120°	4.13	4.2
<i>p</i> - " " .	"	"	180°	4.33	4.5

are in better agreement with the observed values, but there are still considerable deviations to be accounted for. Another factor which should be taken into consideration, but concerning which there is very little information available, is the spatial distortion resulting from the proximity of two polar groups. The angle  $\theta$  between the directions of application of the dipole moments of groups in the *o*-position to one another may thus be greater or less than the ideal value of 60°. A remarkable example of the mutual influence of groups in the *o*-position, sometimes called the "ortho effect," is the observation that the dipole movement of 1, 2, 4, 6-



tetrachlorobenzene is 0.65 (Hassel and Naeshagen, 1931), whereas the calculated value is 1.56.

**Dipole Moments of Linkages.** Strictly speaking it is not justifiable to refer to the dipole moment of a group or radical; every dipole is associated with a *linkage* and each one of these possesses a partial moment which contributes vectorially to the resultant moment of the molecule. Eucken and Meyer (1930) have made an attempt to analyse the dipole constituents of a molecule in detail and have taken into consideration the directions of operation of the constituents. The individual moments deduced for various linkages are given in Table XXXVIII.; the left-hand component, as written, is positive with respect to the other.

TABLE XXXVIII

*Dipole Moments of Linkages (Eucken and Meyer)*

Radical . . .	C—C	H—C	C—O—	H—O	C=O	C—Cl
$\mu \times 10^{18}$ . . .	0	0.4	0.7	1.6	2.3	1.5

As an illustration of the method used to calculate the total moment of a molecule, the case of methyl alcohol may be quoted

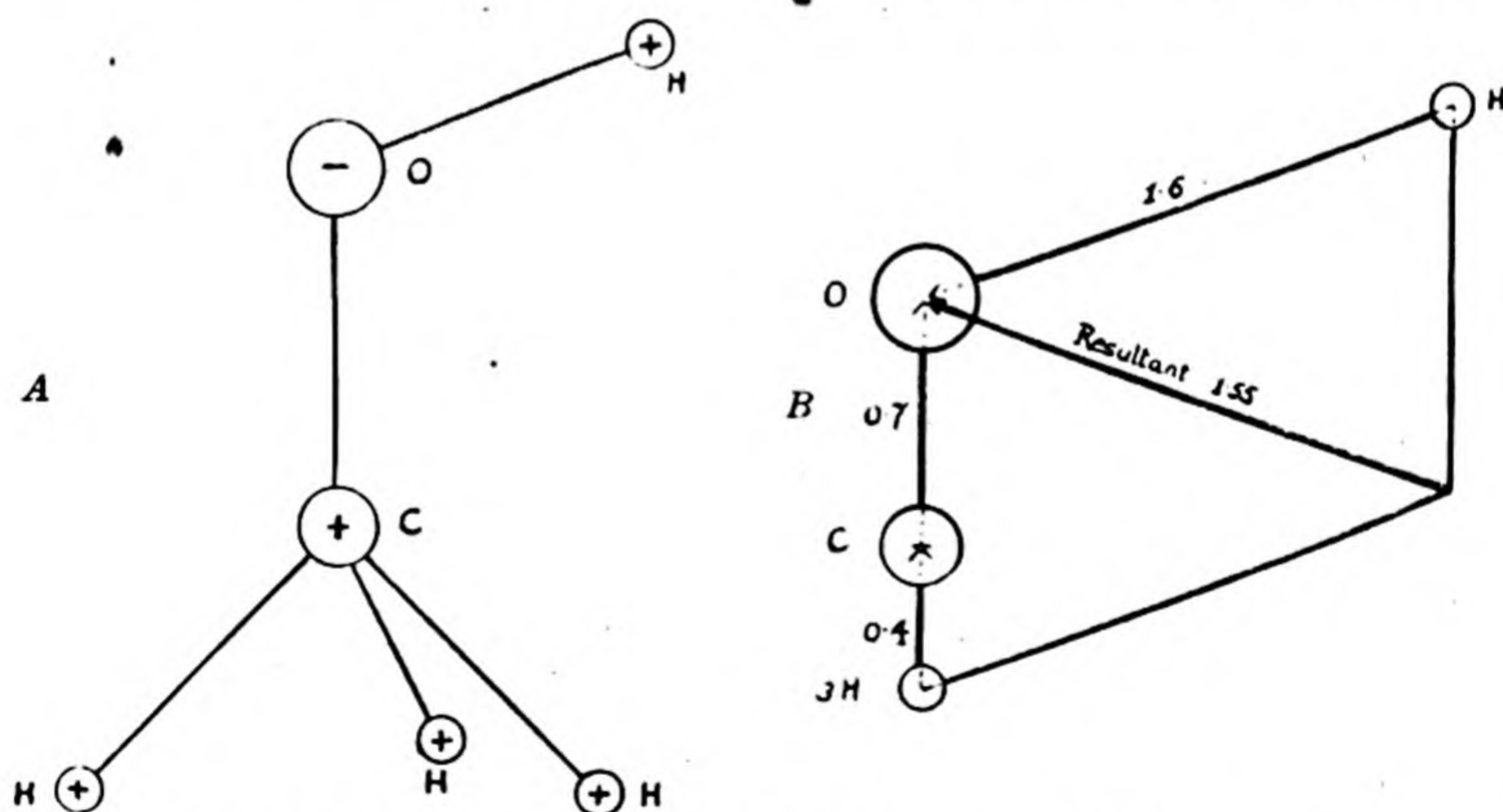


FIG. 8.—Calculation of the dipole moment of methyl alcohol by the vectorial addition of the values attributed to various linkages. (After Eucken.)



from Eucken's book (1930). In Fig. 8, *A*, the constituent atoms of the molecule are drawn with special reference to the valency directions; the angle between the oxygen linkages is taken as  $110^\circ$ . The dipoles corresponding to the various constituent radicals are drawn to scale and in the correct direction in Fig. 8, *B*; the diagonal gives the value of the resultant dipole moment ( $1.55 \times 10^{-18}$ ) determined graphically by the principle of the parallelogram of forces. The values calculated in this manner may be compared with the observed values quoted in Table XXXIX.; the agreement is reasonably good and might be improved if allowance were made for the interaction between dipoles.

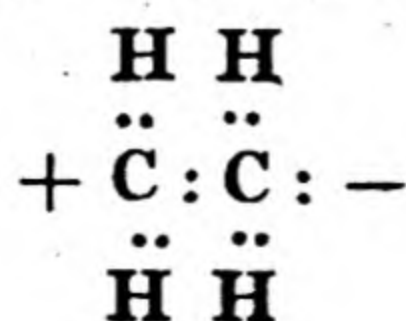
TABLE XXXIX.—*Calculated and Observed Dipole Moments*

Substance.	Calculated Moment.	Observed Moment.
Ethyl chloride . . .	$1.9 \times 10^{-18}$	$1.98 \times 10^{-18}$
Acetaldehyde . . .	2.7	2.7
Alcohols . . .	1.55	1.7
<i>p</i> -Chlorophenol . . .	2.8	2.6
<i>p</i> -Cresol . . .	1.5	1.6
Phenol. . .	1.5	1.7

With *p*-chlorophenol and *p*-cresol the calculated dipole moments would have been 3.2 and 1.3, respectively, if the inclination of the —OH dipole to the plane of the benzene ring had not been taken into consideration.

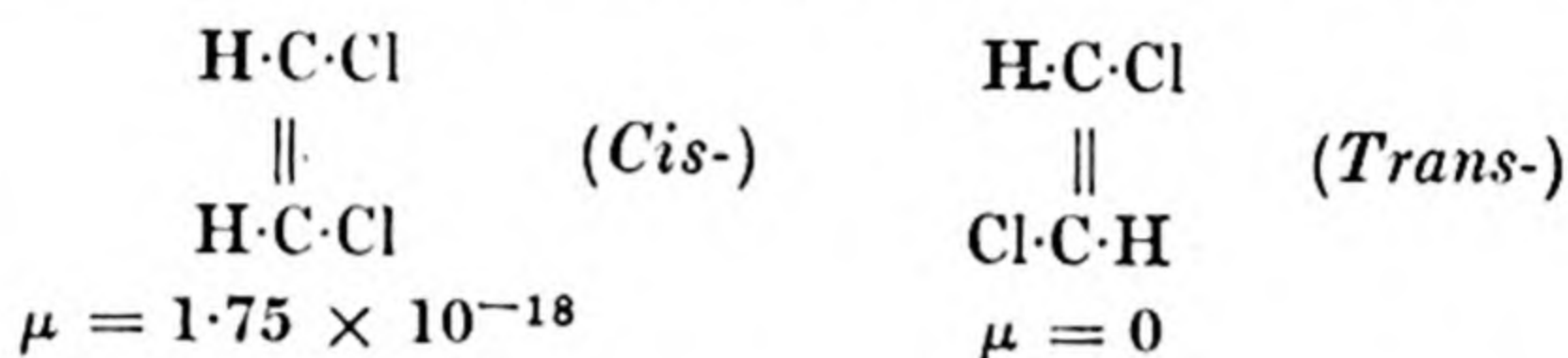
### DEVIATION EFFECTS

**Ethylene Derivatives.** It will be observed that in Table XXXIII., p. 150, the dipole moment of ethylene is given as  $0.5 \times 10^{-18}$ ; this value, although small, is unexpected. In order to account for it the suggestion has been made that ethylene may contain a semi-polar double bond (p. 16), and have the structure





If this were the case the two carbon atoms would be really joined by a single linkage about which free rotation should be possible ; this rotation, however, does not occur, as the dipole moments for dichloroethylene in the *cis*- and *trans*- forms clearly indicate. The values obtained by Errera (1926) and others are



If there were free rotation it is doubtful if such a clear cut difference could have been obtained ; it appears, therefore, that in ethylene only a small fraction, if any, of the molecules can contain the semi-polar bond. It is not improbable that the measured dipole moment is incorrect, since errors to the extent of  $0.5 \times 10^{-18}$  e.s.u. have been detected in other observations ; for example, the dipole moment of naphthalene was at one time given as  $0.8 \times 10^{-18}$ , but is now stated to be zero. The small moment reported for  $\alpha$ -butylene,  $0.37 \times 10^{-18}$  e.s.u., may be real, since its constitution is represented by  $\text{H}_2\text{C} : \text{CH}\cdot\text{CH}_2\cdot\text{CH}_3$ , and the effect of two hydrogen atoms on one of the double-bonded carbon atoms may very well be slightly different from that of a hydrogen atom and an ethyl group on the other.

The calculated dipole moment of *cis*-dichloroethylene is  $2.55 \times 10^{-18}$  as compared with the experimental value of  $1.75 \times 10^{-18}$  ; similar discrepancies have been found for *cis*-dibromoethylene and *cis*-diiodoethylene ; for these substances the observed moments are  $1.35$  and  $0.76 \times 10^{-18}$  respectively, whereas the calculated values are  $2.45$  and  $2.12 \times 10^{-18}$ . de Bruyne, Davis and Gross (1932) have collected data showing that substances in which the dipolar group is attached to a double-bonded carbon atom have moments smaller than those calculated, and they suggest the possibility of the group  $=\text{C}-\text{H}$  possessing an equivalent moment of 0.5.

Bergmann and Engel (1931) consider that there is appreciable distortion of the valency angles in the substances under discussion on account of the repulsion of the two polar groups ; the increase



of the discrepancy between observed and calculated values from 0.8 in the chloro- to 1.36 in the iodo-compound apparently favours this view, but the effect of dipole induction is likely to be important, as will appear shortly.

**Dipole Induction of Linkages.** The marked influence of the dipole induction of one linkage on another is seen in connection with the chloromethanes. The dipole moment of methylene chloride,  $\text{CH}_2\text{Cl}_2$ , should be, according to Thomson's equation (xxix.),  $2 \cos \frac{1}{2}(109^\circ 28')$ , *i.e.*, 1.155 times the value for methyl chloride; on the same basis the moment for chloroform should be the same as that of the monochloro-compound. The calculated values are 2.2 and 1.85 Debye units for methylene chloride and chloroform, respectively, compared with the observed values of 1.5 and 1.1*D*. It was thought at one time that the difference was to be attributed to an increase in the Cl—C—Cl valency angle because of the mutual repulsion of the chlorine atoms; the results obtained by Bewilogua (1931), using the X-ray diffraction method with the vapours, indicated that the actual values were  $124^\circ \pm 6^\circ$  and  $116^\circ \pm 3^\circ$ , respectively, whereas angles of  $130^\circ$  and  $116^\circ$  were required to account for the observed moments. New measurements by the electron-scattering method ("Recent Advances in General Chemistry," Chapter V.) have shown that the valency angles are really very little different from the tetrahedral value, so that the explanation previously advanced to account for the abnormal dipole moments of methylene chloride and chloroform is not tenable (Sutton and Brockway, 1935). It must be concluded, therefore, that the abnormality is due to the induced effect of one C—Cl bond on another (Smyth and McAlpine, 1933). When two polar moments, operating in the same sense, are more or less parallel, as in the halogeno-methanes, each induces a dipole in the other in the opposite sense to the primary moment, so that the latter is effectively decreased. In the examples considered the reduction is evidently as large as 30 per cent. of the original bond moment, and if similar decreases occur in the halogeno-ethylenes considered above, the differences between observed and calculated moments can be accounted for, to a great extent.



**Aliphatic and Aromatic Compounds.** It has been realised that the dipole moment of a group might vary according as it was attached to an alkyl or an aryl residue, but the work of Sutton (1931) has shown that the difference may have an important significance. He compared the dipole moments of various benzene derivatives,  $C_6H_5 \cdot X$  with the corresponding *tertiary*-butyl compounds  $(CH_3)_3C \cdot X$ ; Sutton considered that by using the  $(CH_3)_3C$  radical as a standard any influence on the dipole moment due to induced effects would be the same in alkyl and aryl compounds, since in both cases the carbon atom to which X is attached is joined only to other carbon atoms. It was found that the substituents could be arranged into two groups, viz.,  $CH_3$ , O,  $NH_2$ , Cl, Br, I, and  $CH_2Cl$  in one, and  $CCl_3$ ,  $COCH_3$ , CO, CN and  $NO_2$  in the other, with  $CHCl_2$  as intermediate. For radicals in the first group the quantity  $\mu_{aryl} - \mu_{alkyl}$  is negative,\* and this means that electrons are drawn away from the dipolar group into the benzene nucleus, whereas in the second group  $\mu_{aryl} - \mu_{alkyl}$  is positive, which implies a drift of electrons away from the nucleus. It is known that radicals belonging to the first group, when substituted in a benzene ring, direct further substituents in the ortho- and para-positions, to account for which the so-called "mesomeric" part of the "tautomeric" effect, resulting in the drift of electrons into the nucleus, has been postulated by organic chemists; the second group are meta-directing, causing electrons to move away from the benzene ring. In view of the parallelism with the results of dipole measurements Sutton has concluded that the quantity  $\mu_{aryl} - \mu_{alkyl}$  is an actual quantitative measure of the electromeric effect; it is supposed to indicate the extent and direction of the electron displacement in the nucleus resulting from the introduction into it of the substituent group X. Although this suggestion is attractive and plausible it is open to criticism; one objection is that the most recent results (Groves and Sugden, 1935) show that there is no quantitative relationship between the directive power of a group and the difference between the moment in aryl and alkyl compounds. Incidentally it may not be without

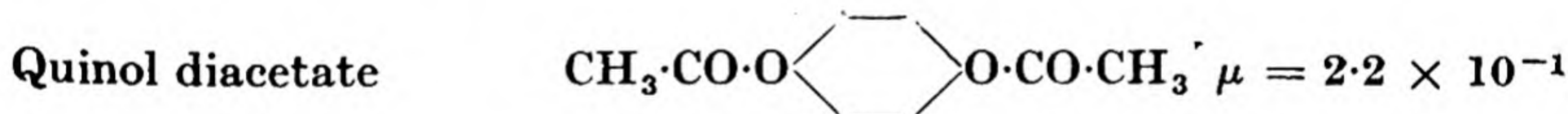
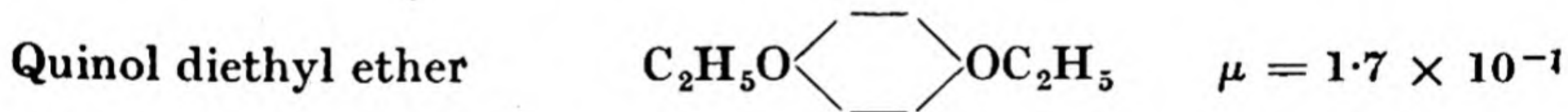
\* The differences as given here are arithmetical, and do not include the sign of the dipole moment.



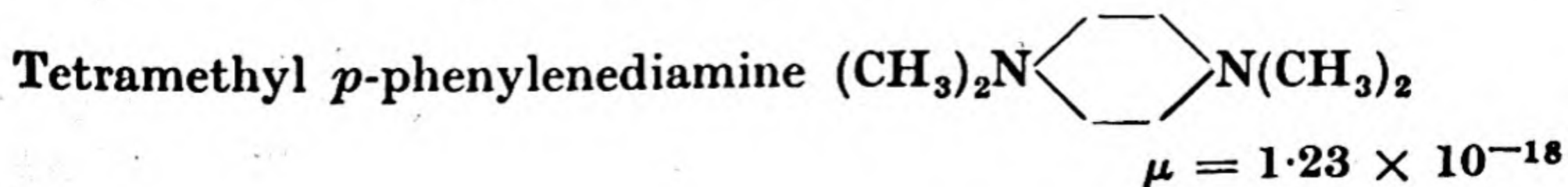
significance that the order of increasing values of  $\mu_{\text{aryl}} - \mu_{\text{alkyl}}$  agrees roughly with the order of increasing negative dipole moments; in view of the well-known polarisability of the conjugated double bond system in the benzene nucleus it is not improbable, therefore, that the effects observed may be due to induction. The claim that this factor has been eliminated by comparing phenyl and *tertiary*-butyl compounds does not appear to be convincing.

### ABNORMAL RESULTS

**Para-Compounds.** It will be seen from Table XXXIII. that *p*-dichloro- and *p*-dinitro-benzene have zero moments, and this is also the case for *p*-xylene and *p*-dibromo-benzene; such a result is to be expected if the benzene nucleus lies flat, since the two dipoles will be exactly equal and act in diametrically opposite directions. Certain *p*-compounds with two identical groups do, however, possess a definite dipole moment; for example,

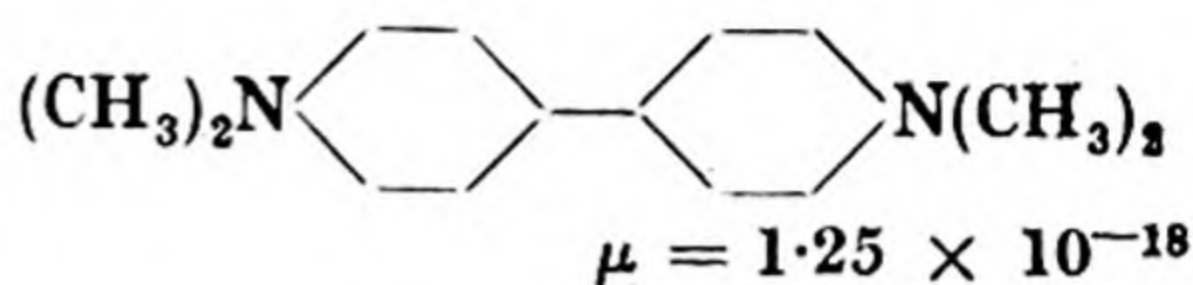


whereas a zero value might have been expected in each case. This type of abnormality has been found with all substance containing an  $-\text{O}\cdot\text{X}$  group attached to the benzene nucleus, where X may be H, an alkyl group, or an acyl radical, *e.g.*,  $\text{CH}_3\cdot\text{CO}$ , and in many other cases where the substituent group contains an oxygen atom, *e.g.*,  $-\text{CHO}$ ,  $-\text{CO}\cdot\text{OCH}_3$ . It also occurs when the  $-\text{NH}_2$ ,  $-\text{NHR}$  or  $-\text{NR}_2$  groups are present, for example





Tetramethyl benzidine



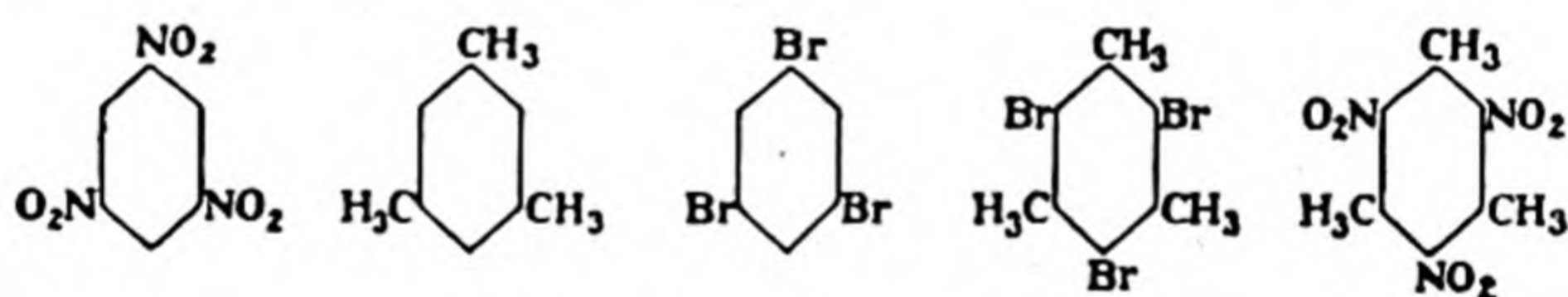
The same difference between calculated and observed values is found for *p*-compounds in which the two groups are different, but one is of the type under discussion ; some instances are quoted in Table XL.

TABLE XL

*Observed and Calculated Dipole Moments for p-Compounds*

Substance.	$m_1$	$m_2$	$\mu$ calc.	$\mu$ obs.
<i>p</i> -nitrobenzaldehyde	- 3.9	- 2.8	$1.1 \times 10^{-18}$	$2.4 \times 10^{-18}$
<i>p</i> -nitraniline .	- 3.9	+ 1.5	5.4	7.1
<i>p</i> -chlorophenol .	- 1.5	- 1.7	0.2	2.4
<i>p</i> -nitrophenol. .	- 3.9	- 1.7	2.2	5.1

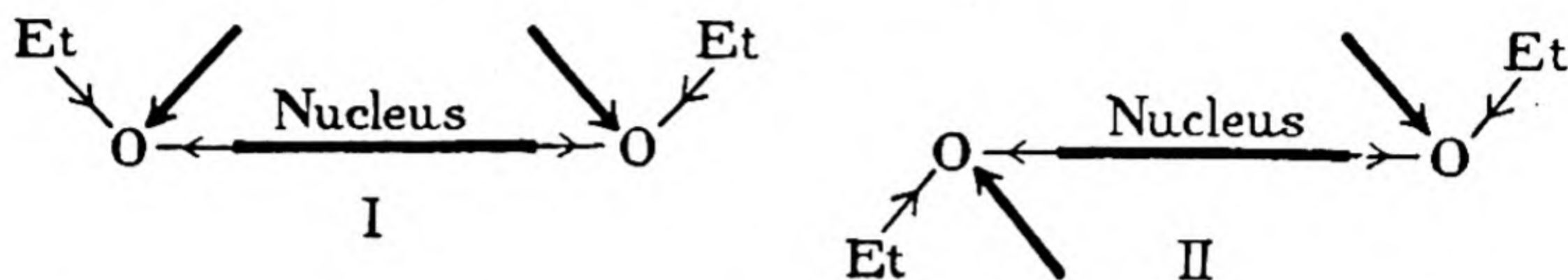
**Oxygen Derivatives.** It was first supposed that the explanation might be found in the supposition that the benzene ring was not planar, but this view is improbable, as so many *p*-compounds, and symmetrical tri-substituted derivatives of mesitylene and benzene, *e.g.*,



have zero moments. The alternative view, which has been widely adopted recently, is that when the substituent group is attached to the benzene ring by means of an oxygen or a nitrogen atom the dipole vector does not operate in the plane of the nucleus. This is just what might have been expected from a careful consideration of the triangular structure for the water molecule, and the three-dimensional model for ammonia. If the two valencies of oxygen are always inclined at  $110^\circ$  the configuration of the apparently abnormal quinol diethyl ether, for example, may be



represented by either of the formulæ I. or II. (below); these actually represent extreme positions, since the — OEt group can rotate freely about the bond joining the oxygen atom to the nucleus, and all intermediate stages should be possible.



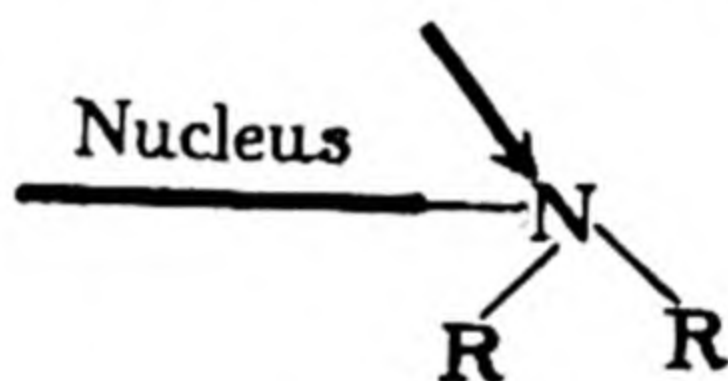
The moment of the — OEt group may be considered as made up of two separate moments: one due to  $(C_6H_4) - O$  acting in the plane of the nucleus, and the other to  $O - (Et)$  inclined at an angle of  $110^\circ$  to the former. The resultant moments, shown by thick arrows, for the two — OEt groups will then be either inclined at an angle of approximately  $90^\circ$  (I), or else parallel to one another (II), in the extreme cases; in the former instance the net moment of the molecule is about  $2.0 \times 10^{-18}$  e.s.u., and in the latter zero. The actual dipole moment of the compound is  $1.7 \times 10^{-18}$ ; this value will be considered later, p. 170, from the standpoint of the influence of "free rotation" on the dipole moment.

**The Tetrahedral or Pyramidal Carbon Atom.** Another aspect of the deviation of the line of the dipoles from that joining the group to a carbon atom is of interest in connection with a controversy, which arose about 1925, concerning the tetrahedral arrangement of groups in space around a carbon atom. As a result of the X-ray examination of pentaerythritol  $C(CH_2OH)_4$  it was concluded, erroneously, that the central carbon atom was at the apex of a pyramid and the —  $CH_2OH$  groups all in one plane. This revolutionary suggestion appeared to obtain support from the observation that the compounds  $C(OCH_3)_4$ ,  $C(OC_2H_5)_4$  and  $C(CH_2 \cdot O \cdot COCH_3)_4$  all possessed permanent dipole moments. If the structure of the carbon atom were tetrahedral, then compounds of the type  $CX_4$  should be quite symmetrical and have no resultant moment, but if the atom is pyramidal then a moment should be found in *all* such compounds. As a matter of fact  $CH_4$ ,  $CCl_4$ ,

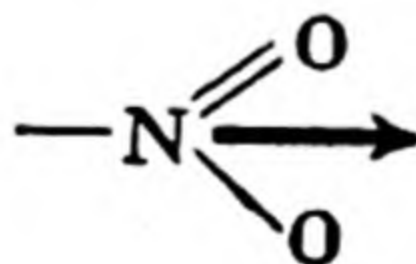


$C(NO_2)_4$  and  $C(CH_2Cl)_4$  all have zero moment, and so it was clear that in these cases, at least, the tetrahedral structure was applicable. In the other instances it will be noted that the polar groups all contain oxygen atoms, and the moments of these groups do not act along the line joining them to the central atom; the molecule then has a net dipolar moment, even though the arrangement of the groups is tetrahedral, and there is no reason to assume a pyramidal structure.

**Nitrogen Derivatives.** The fact that the moment of the substituent group does not act along the line joining the group to the benzene nucleus also accounts for the apparent anomalies observed with compounds containing  $-NR_2$  or  $-NH_2$  groups. The configurations of such groups may be represented by

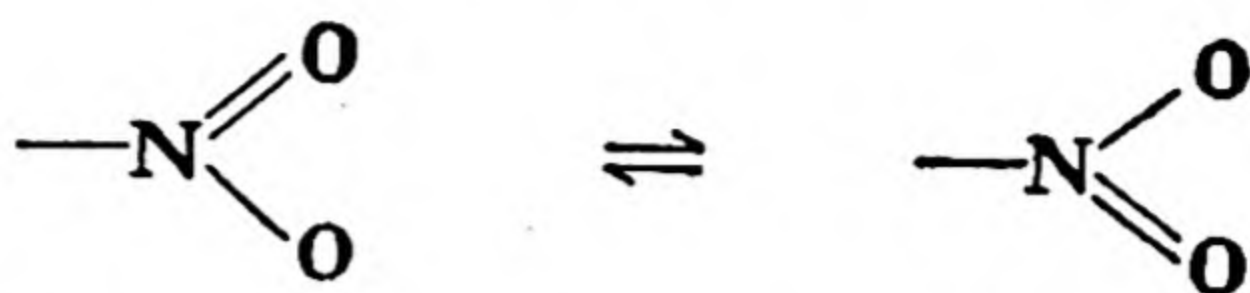


the direction of the dipole (thick arrow) being more or less perpendicular to, and not in, the plane of the benzene ring. It may appear strange that the nitro-group ( $-NO_2$ ) does not behave exceptionally, but gives a dipole acting in the same direction as the line joining the group to the nucleus (see Table XXXVII.). In ammonia and in amines the nitrogen has a lone pair of electrons and shares six electrons with three other atoms, but in the nitro-group all eight electrons of the nitrogen octet are shared; in the latter this must result in a symmetrical configuration, so that the dipole due to the  $NO_2$  group acts in the line of the remaining nitrogen valency, thus



This result apparently means that the group contains a valency bond, *i.e.*, a pair of electrons, which oscillates between the two oxygen atoms, thus





so that there is a resultant symmetry. Alternatively, it may be supposed that the two structures depicted are resonating states (p. 92), so that in the actual molecule both oxygen atoms are attached to the nitrogen in the same manner.

### FREE ROTATION OF DIPOLAR GROUPS

It might have been anticipated on a preliminary consideration that a symmetrical compound of the type  $\text{XCH}_2\cdot\text{CH}_2\text{X}$  would have zero dipole moment; further examination shows, however, that this is not so. Since X is different from H the resultant moment of the three linkages C—H, C—H and C—X, making up the  $-\text{CH}_2\text{X}$  group cannot lie in the same direction as the C—C bond; the constituent dipoles of the molecule may consequently

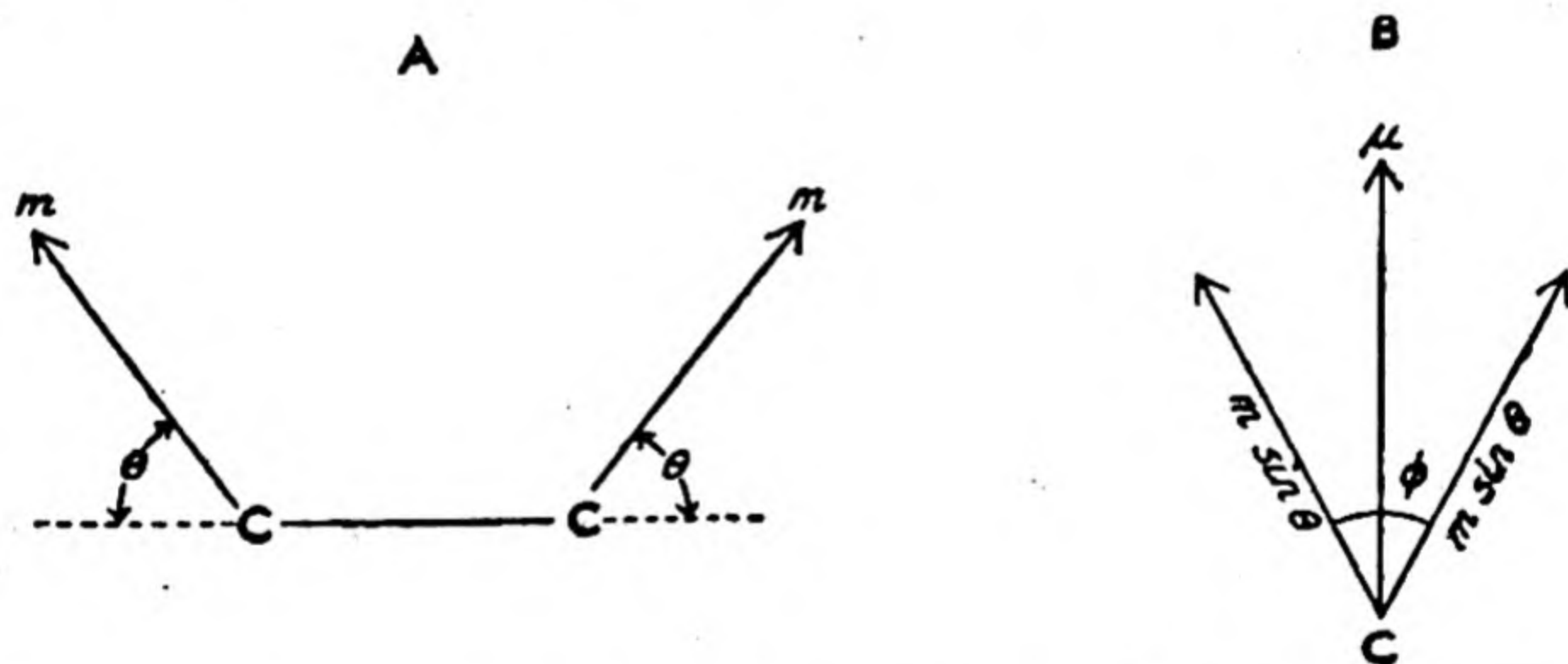


FIG. 9.—Calculation of the resultant moment of two similar groups capable of free rotation about the C—C linkage.

be represented as in Fig. 9A, the arrows showing the direction of the  $-\text{CH}_2\text{X}$  group moment ( $m$ ).

It must be remembered further that, owing to the possibility of free rotation about the C—C bond, the position shown in Fig. 9A is only one of an infinite number of possibilities; actually both the arrows representing the group moments may be imagined as rotating continuously round a solid angle. The components of



these moments along the C—C axis will be  $m \cos \theta$  in opposite directions and so will cancel one another, and both  $-\text{CH}_2\text{X}$  groups will have a component  $m \sin \theta$  at right angles to the C—C linkage. At any particular instant, however, these components will be inclined at an angle  $\phi$  to one another, so that the position as viewed in the direction of the C—C line, that is at right angles to Fig. 9A, will be as represented in Fig. 9B. The resultant effective moment  $\mu$  may then be calculated (Williams, 1928) by assuming that one of the components is fixed whilst the other can take up all possible positions relative to it, each of these positions being equally probable. This leads to the expression

$$\mu^2 = \frac{1}{2\pi} \int_0^{2\pi} (2m \sin \theta \cos \phi/2)^2 d\phi \quad . \quad . \quad . \quad (\text{xxx.})$$

and so 
$$\mu = m\sqrt{2} \sin \theta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (\text{xxxi.})$$

To test the applicability of this equation a specific case, namely, that of ethylene dichloride, may be considered. The moment of the  $-\text{CH}_2\text{X}$  group is about  $1.6 \times 10^{-18}$ , and the angle at which it acts with respect to the C—C bond is probably somewhat greater than the tetrahedral angle, and consequently  $\theta$  may be assumed to have a maximum value of about  $70^\circ$ ; it follows, therefore, that if there is absolutely free rotation without restriction about the C—C bond the dipole moment of ethylene dichloride should be approximately  $2.1 \times 10^{-18}$ , whereas the observed value, in benzene solution is  $1.8 \times 10^{-18}$ . The discrepancy is not very great, but it may have some significance, as will appear later.

The formula developed for calculating the effective moment of compounds of the type  $\text{XCH}_2\cdot\text{CH}_2\text{X}$  may be used in connection with the hydroquinone ethers,  $\text{RO}\cdot\text{C}_6\text{H}_4\cdot\text{OR}$ , in which free rotation leading to different configurations is possible (p. 167). In Fig. 9A the C—C line may be taken as representing the plane of the benzene nucleus and the arrows as giving the direction of the O—R linkage, the rotation occurring about the  $>\text{C—O}$  bond; the moments of the two  $>\text{C—O}$  linkages acting in exact opposition cancel one another. For hydroquinone diethyl ether, assuming the O—Et link to have a moment of  $1.1 \times 10^{-18}$  and the oxygen



valency angle to be  $110^\circ$ , the resultant moment, assuming free rotation, is  $1.46 \times 10^{-18}$  in comparison with the experimental value of  $1.7 \times 10^{-18}$ .

If the compound in which free rotation is possible is not of the symmetrical type, *e.g.*,  $\text{XCH}_2\cdot\text{CH}_2\text{X}'$  or  $\text{RO}\cdot\text{C}_6\text{H}_4\cdot\text{OR}'$ , then it has been shown by Fuchs (1931) that the effective moment of the compound, using the Williams method, is given by

$$\mu = \sqrt{m_1^2 + m_2^2 - 2m_1m_2 \cos \theta_1 \cos \theta_2} \quad . \quad (\text{xxxii.})$$

where  $m_1$  and  $m_2$  are the moments of the two constituent dipoles, and  $\theta_1$  and  $\theta_2$  are the respective angles they make with the C—C bond or with the plane of the benzene ring.

**Free Rotation and Potential Energy.** Meyer (1930) has made a more complete study of the effect of free rotation on the dipole moment by taking into consideration the mutual potential energy of the two rotating dipoles; he considers that if this energy is appreciably less than the energy of thermal agitation  $kT$ , where  $k$  is the Boltzmann constant, then rotation can occur quite freely without hindrance and the formulæ given above (equations xxxi. and xxxii.) are applicable. If, however, the mutual potential energy exceeds this value, then free rotation is hindered and certain positions relative to one another of the two constituent groups will be preferred over others; the observed dipole moments will then be less than the calculated values, because the repulsion of the groups will tend to make them take up positions in which their moments oppose one another (*cf.* p. 167, formula II). For such substances, however, as the temperature is raised the increased energy of rotation, or rather oscillation, will tend to overcome the effect of the mutual potential energy of the dipoles so that the resultant moment will increase until the calculated value for completely free rotation is reached. Meyer has made an approximate estimate of the distances between dipolar groups at which they begin to influence one another; when the group moment is  $1 \times 10^{-18}$  then the distance apart must not exceed  $3 \times 10^{-8}$  cm. if free rotation is to occur; for moments of 2 and  $3 \times 10^{-18}$  the minimum distances are 4.5 and  $6 \times 10^{-8}$  cm. respectively.



**Partially Restricted Rotation.** For ethylene dichloride it appears that the mutual potential energy of the two rotating groups is about  $2-3 kT$ , and so free rotation will be hindered—the group moment is  $1.5 \times 10^{-18}$  and the distance apart of the Cl atoms is  $3 \times 10^{-8}$  cm.—and the dipole moment should increase with increasing temperature. In benzene solution  $\mu$  is  $1.8 \times 10^{-18}$  and appears to be independent of temperature, but in hexane solution the value increases from  $1.26 \times 10^{-18}$  at  $-75^\circ$  to  $1.42 \times 10^{-18}$  at  $40^\circ$  (Meyer, 1930), and in heptane solution it changes from  $1.16 \times 10^{-18}$  at  $-50^\circ$  to  $1.42 \times 10^{-18}$  at  $50^\circ$  (Smyth, 1931). The molecules of benzene appear to have some influence in weakening the forces between the rotating dipoles, so that in this solvent the dipole moment is greater, and the temperature coefficient is evidently reduced to such an extent that it appears to be zero. The environment probably affects the mutual potential energy of the dipoles so that the resultant moment will, in any case, be dependent on the nature of the solvent.

The moment of ethylene dichloride has also been studied in the vapour state by Zahn (1931) and by Greene and Williams (1932), using the temperature method (p. 138); although the actual values by the different authors are not the same, because of the modifications which become necessary in equation (xv.) under these conditions, the results indicate quite clearly that the dipole moment increases with temperature. For example, Greene and Williams find  $\mu$  is  $1.27 \times 10^{-18}$  at  $25^\circ$  and  $1.57 \times 10^{-18}$  at  $315^\circ$ . Similar variations of the dipole moment with temperature have been found for ethylene dibromide and for ethylene chlorobromide, both in solution and as vapours.

Hydrogen peroxide and hydrazine are compounds in which partially restricted rotation is to be expected, although measurements of their dipole moments over a range of temperature have not yet been made. There is no doubt, however, from the calculations of Penney and Sutherland (1934), already described (p. 75), that rotation is not free; the molecules tend to take up a more or less definite configuration at ordinary temperatures. In hydrogen peroxide, for example, the two H·O—O planes make an angle of about  $100^\circ$  with one another, and the oxygen valency angle is



also about  $100^\circ$ . The calculated dipole moment, based on the known bond moment of the O—H linkage, from water, is  $2.0D$ , compared with the observed value  $2.13D$ . Hydrazine has a similar configuration, the observed and calculated dipole moments being  $1.83D$  and  $1.70D$ , respectively.

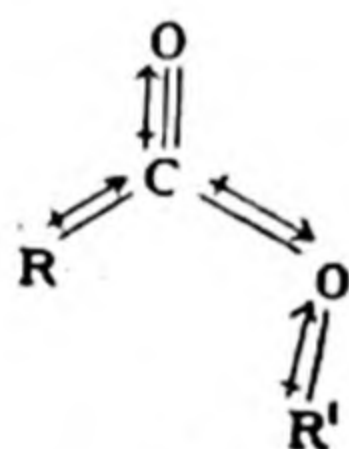
**Unrestricted Rotation.** The mutual potential energy of the rotating groups in hydroquinone diethyl ether is very much smaller than  $kT$ , since the —OEt groups are separated by at least  $6 \times 10^{-8}$  cm. and the group moments are only  $1.1 \times 10^{-18}$ . In this compound completely free rotation should be possible and the resultant moment should be equal to the value calculated from equation (xxxi.) and be independent of temperature; in spite of previous conclusions to the contrary, it is now accepted that the dipole moment of hydroquinone diethyl ether is  $1.73 \times 10^{-18}$  and does not vary with temperature. As already shown, the calculated moment is  $1.46 \times 10^{-18}$ , but the discrepancy may be due to an error in the moment assumed for the O—Et linkage; this is highly probable, since the observed value for the ether is greater than that calculated, whereas any restriction of rotation would have made it smaller.

An analogous case is that of *p*-xylylene dichloride,  $\text{CH}_2\text{Cl} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2\text{Cl}$ , which should behave like ethylene dichloride in which the rotation is unrestricted, because the — $\text{CH}_2\text{Cl}$  groups have been separated by  $6 \times 10^{-8}$  cm. Taking the moment of this grouping as  $1.85 \times 10^{-18}$  e.s.u., the moment of benzyl chloride, the value calculated for the *p*-xylylene dichloride, assuming free rotation, is  $2.26D$ , compared with the observed value of  $2.23D$ ; the agreement in this case is very striking (de Bruyne, *et al.*, 1933).

It is noteworthy that in the series  $\text{Br}(\text{CH}_2)_n\text{Br}$  the temperature effect on the dipole moments decreases and eventually becomes negligible as the distance between the Br atoms is increased; thus Smyth and Kamerling (1931) found  $\mu$  for decamethylene bromide ( $n = 10$ ) to vary only from  $2.69$  at  $0^\circ$  to  $2.75 \times 10^{-18}$  at  $80^\circ$ . The separation of the ends of the molecule is now so great that the restriction to free rotation which occurs in ethylene dibromide ( $n = 2$ ) has completely disappeared.

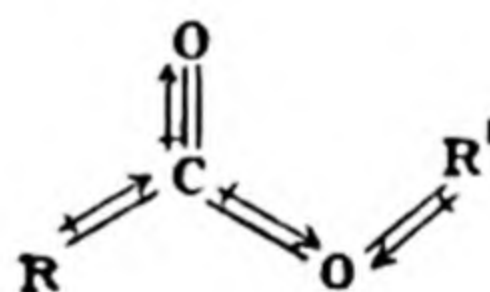


**Carboxylic Acids and Esters.** In addition to the two types of behaviour discussed, namely (a) restricted rotation and variation of  $\mu$  with temperature, and (b) free rotation with no temperature effect, there are certain molecules in which the mutual potential energy of the dipoles is so great that rotation is restricted to such an extent that increase of temperature has very little influence on the moment under ordinary conditions. In such compounds, *e.g.*, carboxylic acids, in which the mutual potential energy of the  $-\text{CO}$  and  $-\text{OH}$  groups is about  $10 kT$ , the observed dipole moment is very appreciably less than the calculated value yet does not vary with temperature. Meyer (1931) has calculated that acetic acid would have to be heated to  $20,000^\circ$  before the groups could rotate freely, and so it is not surprising that for the temperature limits within which measurement is possible the dipole moment is found to be constant. The same high mutual potential energy occurs in esters; the extreme configurations resulting from free rotation about the  $\text{C} - \text{O}$  bond would be



I.

$$\mu(\text{cal.}) = 3.4 \times 10^{-18}.$$



II.

$$\mu(\text{cal.}) = 1.1 \times 10^{-18}.$$

These may be termed *cis*- (I) and *trans*- (II) positions. Eucken and Meyer have summed vectorially the four dipoles involved in the molecule of  $\text{R} \cdot \text{COOR}'$  and found that the respective moments should be  $3.4 \times 10^{-18}$  for formula I. and  $1.1 \times 10^{-18}$  e.s.u. for formula II. These values are independent of the nature of R and R' provided they are hydrogen atoms or alkyl groups only, since the moment of  $\text{H} - (\text{C})$  should be the same as of  $\text{CH}_3 - (\text{C})$ , or of  $\text{CH}_3 \cdot [\text{CH}_2]_n - (\text{C})$ . The dipole moments of fatty acids are approximately  $1.4 \times 10^{-18}$  and of most esters about  $1.8 \times 10^{-18}$  (Müller and Sack, 1930; Smyth and Walls, 1931; Donle, 1931; Wolf and Gross, 1931); these values seem to vary very little, if at



all, with temperature. It is clear that owing to the interaction of the groups in acids and esters rotation is prevented and the groups oscillate about a mean configuration of minimum potential energy; this configuration approaches the *trans*- position (II.) representing a repulsion between the similar R and R groups, and an attraction of the oppositely charged = O and R.

**Combined Free and Restricted Rotation.** In view of the restricted rotation which occurs in ethylene dibromide and dichloride it is perhaps surprising to find that the dipole moments of ethylene glycol, chlorohydrin and diamine are independent of temperature (Zahn, 1932; Smyth and Walls, 1932), although the values are less than those calculated for unrestricted rotation. It is highly probable that in these substances two factors are operative: the first of these is the interaction between the two dipolar groups, *e.g.*, —O—H in ethylene glycol, with the result that rotation about the C—C bond is restricted and the molecules oscillate about a mean configuration close to that which might be called the *trans*- position. The moment would then be very small, or zero, for ethylene glycol and diamine were it not for the completely free rotation still possible about the C—O or C—N linkage respectively. The combination of wholly restricted and entirely free rotations leads to a dipole moment less than the calculated value for quite free rotation but independent of temperature; the observed values are in good agreement with those calculated on the basis of these suggestions.

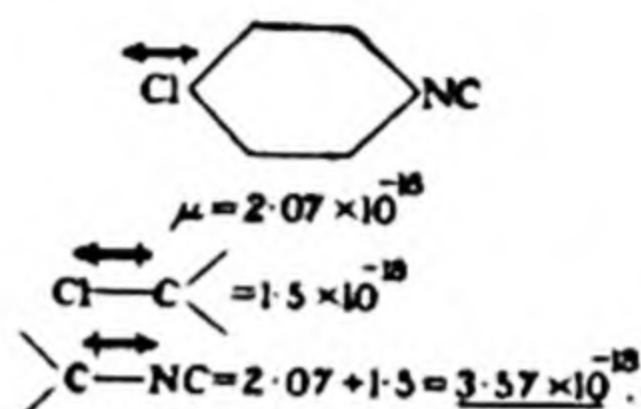
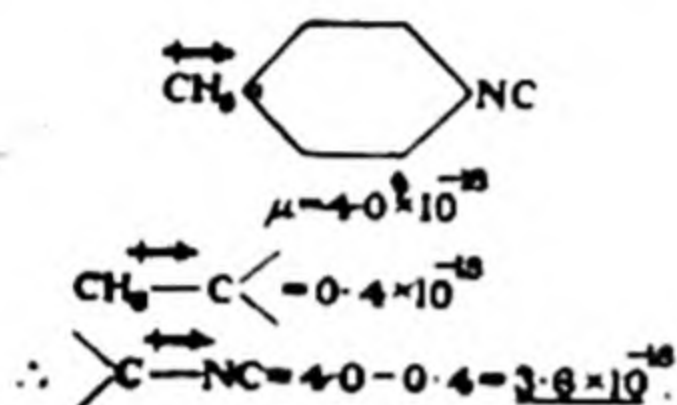
## DIPOLE MOMENTS AND STRUCTURAL PROBLEMS

**Structure of the Isocyanide Group.** An interesting application of dipole moments has been made by Sidgwick (1930) in order to establish the structure of isocyanides. The polar moment of the  $>\text{C}-\text{NO}_2$  and  $>\text{C}-\text{CN}$  linkages, where  $>\text{C}$  represents a benzene ring, may be taken as 3.9 and  $3.84 \times 10^{-18}$  respectively, and since the dipole moment of *p*-nitrobenzonitrile is  $0.66 \times 10^{-18}$ , it may be assumed that the constituent dipoles both act in the same sense, that is, away from the nucleus (cf. p. 157), thus

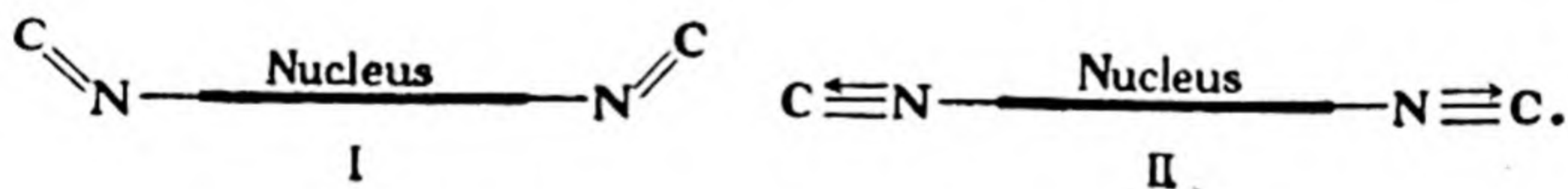




In the nitrile group, therefore, the nitrogen atom is obviously negative with respect to the carbon atom (cf. nitro-group, p. 158). The dipole moments of *p*-tolyl isocyanide and of *p*-chlorophenyl isocyanide have been found to be 4.0 and  $2.07 \times 10^{-18}$  respectively, and from the known values for the  $\text{CH}_3-\text{C}<$  and the  $\text{Cl}-\text{C}<$  bonds the moment of the isocyanide group may be calculated; thus



The moment of the isocyanide group is therefore  $3.6 \times 10^{-18}$ , but the carbon atom is now the negative end of the dipole. The moments produced by the cyanide and isocyanide groups are thus of almost the same magnitude although the signs are reversed; this marked change must imply that in the isocyanide group electrons originally belonging to the nitrogen atom are partially transferred to the carbon, so that the latter becomes negative. The structure of the isonitrile group should consequently be represented as  $-\overset{+}{\text{N}} \equiv \overset{-}{\text{C}}$  or  $-\text{N} \rightleftharpoons \text{C}$ , presumably as the main resonating state. If the alternative  $-\text{N}=\text{C}$  formula were more important the moment of the group would not act in the same direction as the line joining the nitrogen atom to the benzene ring and the polar moment of *p*-diisocyanobenzene,  $\text{CN} \cdot \text{C}_6\text{H}_4 \cdot \text{NC}$  (I.) would be quite large (cf. quinol diethyl ether, p. 167) whereas if the  $-\text{N} \equiv \text{C}$  formula were applicable (II.) the moment would be zero:



An attempt at determining the dipole moment of this compound was made by New and Sutton (1932); the presence of a small amount of a polar impurity made the results somewhat uncertain, and although it cannot be stated that the *measured* dipole moment



of *p*-diisocyanobenzene is zero it is definitely small. If formula I. had been correct the moment of the compound would have been  $2.8 \times 10^{-18}$ .

**Formula of Carbon Monoxide.** A case which is closely allied to that of the isocyanide radical is that of carbon monoxide. If this were strictly  $C = O$ , then a large dipole moment would be expected, as is found in ketones and aldehydes, viz., about  $2.7 \times 10^{-18}$  e.s.u., with the carbon atom positive and the oxygen negative. The actual value for carbon monoxide is, however, very small, and is given in the literature as  $0.12 \times 10^{-18}$  e.s.u. This must mean that electrons have been transferred from the oxygen atom to the carbon in order to neutralise almost entirely the normal value attributed to the  $C = O$  group. The formula for carbon monoxide should therefore be written  $C \equiv O$  or  $\overset{-}{C} \equiv \overset{+}{O}$ ; this conclusion is in harmony with that reached from a study of the spectrum and the parachor of carbon monoxide (see pp. 115, 254), although the resonance concept suggests that the  $C = O$  structure plays some part.

**The Configuration of the Allene System.** It had been shown by van't Hoff that one of the consequences of the tetrahedral carbon atom was that allene derivatives of the type  $abC = C = Cab$  should be resolvable into optical enantiomerides, but many attempts to affect their resolution had failed. As a result it had been suggested (Faltis, 1930) that instead of the two pairs of substituents *ab* lying in planes perpendicular to one another, as the van't Hoff theory required, they were in the same plane so that optical isomerism was not possible, although *cis-trans*-isomerides should exist. In order to distinguish between the two possibilities Bergmann and Hampson (1935) studied the dipole moment of  $\alpha\gamma$ -di-(*p*-bromophenyl)- $\alpha\gamma$ -diphenylallene,  $C_6H_4Br \cdot CPh : C : CPh \cdot C_6H_4Br$ , and found a value of  $1.92D$ , and this was compared with the moments calculated for the structures which would result from the alternative allene configurations. The moment for  $-C_6H_4Br$  was taken as  $1.49D$ , and the angle between the two phenyl groups joined to the same carbon atom was calculated to be  $119^\circ$ , from measurements of the dipole moments of suitable allene compounds (*vide*

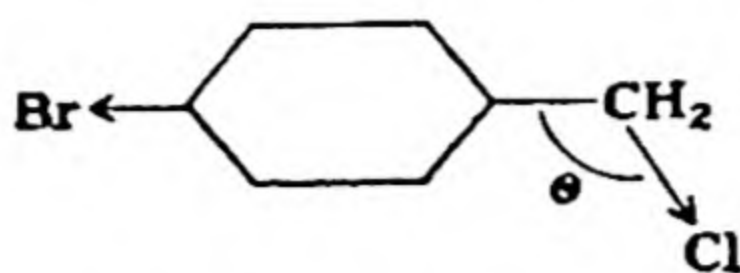


*infra*); from these data the total moment of the bromophenylallene derivative mentioned above was calculated as  $1.85D$ , on the basis of the van't Hoff structure. If the planar configuration had been correct the calculated moments would have been  $2.62D$  for the *cis*-form and zero for the *trans*-form. The dipole moment results indicate therefore that the classical structure is the correct one, and that allene derivatives should be resolvable: it is of interest to record that almost simultaneously with the publication of this work successful resolutions were announced independently in England (Mills and Maitland, 1935) and in America (Kohler, *et al.*, 1935).

**Cis-Trans-Configurations.** The determination of dipole moment provides in some instances a neat, simple and apparently unequivocal method for distinguishing between *cis*- and *trans*-modifications of a given compound; or between *syn*- and *anti*-oximes (Sutton and Taylor, 1931; Barrow and Thorneycroft, 1935). It has been already seen (p. 162) that there is a marked difference between the dipole moments of the *cis*- and *trans*-dichloroethylenes, because in the former case the two C—Cl dipoles enhance one another and in the latter they act in opposite directions, and the same principle can be used in other cases. For example, in order to distinguish between the two oximes of *p*-nitrobenzophenone, they were converted into their *N*-ethers, since the oximes are associated in solution, and the dipole moments measured: the results were  $6.60D$  for the  $\alpha$ -oxime and  $1.09D$  for the  $\beta$ -form. It is evident that in the former case the N→O dipole of the oxime-grouping is operating in the same direction as the same dipole in the nitro-group, and so it is the *syn*-compound, whereas in the  $\beta$ -form the two moments are in opposition and so it must be the *anti*-compound.

**Valency Angles.** Although the valency angle of carbon is well established as  $109^{\circ} 28'$ , provided there is no distortion, there is some uncertainty concerning the angles in oxygen and sulphur compounds; by means of dipole measurements Smyth and Bergmann, and their co-workers, have attempted to throw some light on the subject. The method used may be illustrated by a consideration of *p*-bromobenzyl chloride, viz.,





If  $m_1$  is the moment due to Br, taken as equal to that of bromobenzene ( $1.50 \times 10^{-18}$ ) and  $m_2$  that of Cl in benzyl chloride ( $1.85 \times 10^{-18}$ ) then the resultant group moment is given by equation (xxix.), p. 158, where  $\theta$  is the carbon valency angle. The treatment neglects the influence of the hydrogen atoms of the  $\text{CH}_2$  group, but Smyth has shown that this is justified by the use of the benzyl chloride moment. The observed moment for *p*-bromobenzyl chloride is  $1.72 \times 10^{-18}$ , whence  $\theta$  is calculated as  $119^\circ$ ; from experiments on similar substances in which the Br was replaced by Cl or  $\text{NO}_2$ , and the Cl by Br or CN, the valency angle was found to vary from  $110^\circ$ — $127^\circ$  (Bergmann, Engel and Sándor, 1980), or  $113^\circ$ — $119^\circ$  (Smyth and Walls, 1982). In view of the approximations made Smyth considers that the result does not differ from the tetrahedral angle by more than the probable error of experiments and calculations.

When applying this method to oxygen and sulphur compounds it is necessary to use *p*-derivatives of diphenyl ether or thioether, since otherwise it is not easy to obtain two dipoles acting at the oxygen or sulphur valency angle. From a knowledge of the moment of the ether itself, of *p*- or *pp'*-derivatives and of the corresponding phenyl compounds, it is possible to calculate the required angle. Thus, for bromobenzene, diphenyl ether and *pp'*-dibromodiphenyl ether the dipole moments are 1.50, 1.05 and  $0.6 \times 10^{-18}$  respectively. The angle  $\theta$  is then determined by the equation

$$2 \times 1.50 \cos \theta / 2 - 1.05 = 0.6,$$

which allows for the  $>\text{C}-\text{Br}$  and  $>\text{C}-\text{O}$  dipoles opposing one another; from this it follows that  $\theta$  is  $113^\circ$ . Measurements on other similar compounds have given values for the oxygen valency angle in diphenyl ethers as  $113^\circ$ — $124^\circ$  and in the thioethers  $142^\circ$ — $147^\circ$  (Bergmann, Engel and Sándor, 1980; Smyth and Walls, 1982). These results are unexpectedly large and, although the normal angle may be increased to such an extent as to allow the



two benzene rings to pass one another when rotating about the  $\text{C}_6\text{H}_5 - \text{O}$  or  $\text{C}_6\text{H}_5 - \text{S}$  bond, it is still surprising to find the sulphur angle so much larger than that for oxygen. An examination of the moments of diphenyl ether and its derivatives has shown that the valency angle calculations are rendered invalid by the transmission of polarisation effects across the benzene ring (Bennett and Glasstone, 1934). By making allowance for these interaction effects the dipole moment data lead to the conclusion that the oxygen valency angle is  $128^\circ \pm 4^\circ$  in diphenyl ethers, whereas the sulphur angle in diphenyl sulphides is  $113^\circ \pm 3^\circ$  (Sutton and Hampson, 1935). These results are in harmony with the observations that diphenylene dioxide has zero moment, and consequently has an oxygen angle of at least  $120^\circ$ , whereas the corresponding sulphide, thianthrene, has a moment of about  $1.6D$ , and in it consequently the sulphur angle must be less than  $120^\circ$  (Bennett and Glasstone, 1934).

**Molecular Compounds.** It is possible that dipole moments may find some application in connection with the study of molecular compound formation; this aspect of the subject has hitherto received little attention. Ebert (1925) observed that the polarisation of a mixture of ethyl alcohol and hydrogen chloride was much greater than the sum of the polarisations due to the constituents. This result suggests that the two molecules unite, as is not improbable, to form a highly polar compound. Further, it has been found that *s*-trinitrobenzene, when dissolved in the non-polar solvent benzene, has a definite moment of  $0.8 \times 10^{-18}$  e.s.u.; since the molecule is symmetrical, and the moment of the nitro-group acts either along, or very close to, the line joining the group to the benzene ring, a zero moment is to be expected. The value obtained is too large to be due to experimental error, and Bennett (1929) has suggested that it is due to the presence of a compound of trinitrobenzene and benzene; such a compound is known and an unsymmetrical formula had previously been suggested for it by Bennett and Willis (1929). All molecular compounds of this type will probably have high dipole moments because of the introduction of an additional semi-polar bond; such bonds contribute appreciably to the dipole moment of a molecule. De Vries and



Rodebush (1931) found the moment of diphenyl sulphide ( $1.56 \times 10^{-18}$ ) to be increased to  $4.17 \times 10^{-18}$  in the sulphoxide and to  $5.05 \times 10^{-18}$  in the sulphone, containing one and two semi-polar bonds respectively. Similar results for alkyl compounds have been obtained by Sutton, New and Bentley (1931). Some measurements by Ulich and Nespal (1931) confirm the anticipation of high moments for molecular compounds; the addition products of aluminium and boron trichlorides with various organic substances, containing oxygen or nitrogen capable of donating a pair of electrons to the aluminium or boron sextet (cf. p. 37), were found to have moments of the order of  $6 - 9 \times 10^{-18}$ . Ether and chloroform are known to form compounds in the liquid phase, since the vapour pressures and viscosities of the mixtures are abnormal, and it has been observed that the polarisations of the mixtures are abnormally high. This result has been attributed to the formation of a new linkage in the molecular compound between the oxygen atom of the ether and the hydrogen of the chloroform (Earp and Glasstone, 1935). The increase in dipole moment is by no means as large as that observed for the aluminium and boron compounds already mentioned, but it is definite enough to indicate an electron transfer of some kind.

## REFERENCES

- BENNETT. *Ann. Reports*, 1929, 26, 128\*.  
 BERGMANN *et al.* *Z. physikal. Chem.*, 1930, B8, 111; B10, 106, 397; 1931, B15, 85; 1932, B17, 81, B19, 389, 395, 401; *Z. Elektrochem.*, 1931, 37, 563; *Ber.*, 1932, 65, 446, 457.  
 BERGMANN and HAMPSON. *J. Chem. Soc.*, 1935, 989.  
 BRIEGLER. *Z. physikal. Chem.*, 1930, B10, 205.  
 DE BRUYNE, DAVIS and GROSS. *J. Amer. Chem. Soc.*, 1933, 55, 3936.  
 DEBYE. *Ibid.*, 1912, 13, 97; "Polar Molecules" 1929\*; "The Dipole Moment and Molecular Structure" 1931\*.  
 DE VRIES and RODEBUSH. *J. Amer. Chem. Soc.*, 1931, 53, 2888.  
 Discussion on "Dipole Moments." *Trans. Faraday Soc.*, 1934, 30, 679-904\*.  
 DONLE. *Z. physikal. Chem.*, 1931, B14, 326; 1932, B18, 316.  
 EBERT. *Ibid.*, 1924, 113, 1; 1925, 114, 430.  
 ERRERA. *J. Phys. Radium*, 1925, 6, 390; *Physikal. Z.*, 1926, 27, 764.  
 ESTERMANN and WOHLWILL. *Z. physikal. Chem.*, 1933, B20, 195.  
 EUCKEN and MEYER. *Physikal. Z.*, 1929, 30, 897.  
 FAIRBROTHER. *J. Chem. Soc.*, 1932, 43; 1934, 1840.  
 FRANK. *Proc. Roy. Soc.*, 1935, 152A, 171.  
 FUCHS. *Z. Physikal. Chem.*, 1931, B14, 339.  
 GLASSTONE. *Ann. Reports*, 1935, 32, 126\*.



- GOSS. *J. Chem. Soc.*, 1934, 696.  
 GREENE and WILLIAMS. *Phys. Rev.*, 1932, 42, 119.  
 GROSS. *Physikal. Z.*, 1929, 30, 504.  
 HAMMICK, NEW, SIDGWICK and SUTTON. *J. Chem. Soc.*, 1930, 1876.  
 HASSEL. *Z. Elektrochem.*, 1930, 36, 735; *Z. physikal. Chem.*, 1930, B8, 357; 1931, B12, 79.  
 HØJENDAHL. *Physikal. Z.*, 1929, 30, 891.  
 INGOLD. *Ann. Reports*, 1926, 23, 144\*.  
 JENKINS and SUTTON. *J. Chem. Soc.*, 1935, 609..  
 LE FÈVRE. *J. Chem. Soc.*, 1935, 1747.  
 LOWRY *et al.* *J. Chem. Soc.*, 1930, 782; 1932, 207.  
 MAHANTI. *Physikal. Z.*, 1930, 31, 546.  
 MEYER. *Z. physikal. Chem.*, 1930, B8, 27.  
 MÜLLER. *Physikal. Z.*, 1932, 33, 731; 1933, 34, 689; 1934, 35, 346; 1935, 36, 373.  
 NEW and SUTTON. *J. Chem. Soc.*, 1932, 1415.  
 PARTINGTON *et al.* *Ibid.*, 1931, 2062; 1932, 2812; 1933, 87; 1935, 604.  
 RAMAN and KRISHNAN. *Proc. Roy. Soc.*, 1928, 117A, 589.  
 SÄNGER. *Physikal. Z.*, 1926, 27, 165, 556.  
 SIDGWICK. *Ann. Reports.*, 1931, 28, 367\*.  
 SMALLWOOD. *J. Amer. Chem. Soc.*, 1932, 54, 3048; *Z. physikal. Chem.*, 1932, B19, 242.  
 SMALLWOOD and HERZFELD. *J. Amer. Chem. Soc.*, 1930, 52, 1919.  
 SMYTH *et al.* *Phil. Mag.*, 1923, 45, 849; *J. Amer. Chem. Soc.*, 1925, 47, 1894, 2501; 1927, 49, 1030; 1928, 50, 1536, 1547, 1883; 1929, 51, 1736, 2051, 2380, 3830; 1930, 52, 2227, 3546; 1931, 53, 527, 545, 1296, 2115, 2988, 4242; 1932, 54, 1854, 2261, 4631; 1935, 57, 979; *J. Chem. Physics*, 1933, 1, 190, 247; 1935, 3, 557; *Chem. Reviews*, 1929, 6, 549\*; *J. Ind. Eng. Chem.*, 1931, 23, 1224\*; "The Dielectric Constant and Molecular Structure," 1931\*.  
 SUGDEN. *J. Chem. Soc.*, 1934, 1094; 1935, 971.  
 SUTTON. *Proc. Roy. Soc.*, 1931, 133A, 668.  
 SUTTON and TAYLOR. *J. Chem. Soc.*, 1931, 2190; 1933, 63.  
 ULICH and NESPITAL. *Z. Elektrochem.*, 1931, 37, 559; *Z. physikal. Chem.*, 1932, B16, 153; B17, 21, 369.  
 WALDEN and WERNER. *Ibid.*, 1929, B2, 10.  
 WERNER. *Ibid.*, 1929, B4, 371, 393.  
 WILLIAMS *et al.* *Ibid.*, 1928, 138, 75; 1929, B3, 367; *Physikal. Z.*, 1928, 29, 174; 1930, 31, 363; *J. Amer. Chem. Soc.*, 1926, 48, 1888; 1927, 49, 1676, 2408, 2416; 1928, 50, 94, 362, 2332, 2350; 1930, 52, 557, 1356, 1831, 1838; 1931, 53, 2096; *Chem. Reviews*, 1929, 6, 589\*.  
 WOHLWILL. *Z. Physik.*, 1933, 80, 67.  
 VAN ARKEL and SNOEK. *Z. physikal. Chem.*, 1932, B18, 159.  
 WOLF and FUCHS. Article in Freudenberg's "Stereochemie," 1932, p. 191\*.  
 WOLF and GROSS. *Z. physikal. Chem.*, 1931, B14, 305.  
 ZAHN. *Phys. Rev.*, 1924, 24, 200; 1926, 27, 329, 455; 1928, 32, 497; 1930, 35, 848; 1931, 37, 1516, 38, 321; *Physikal. Z.*, 1932, 33, 400, 525, 686, 730.

\* Review papers and books, wherein further references are to be found, are marked by an asterisk.



## CHAPTER IV

### MOLECULAR SPECTRA

**Band Spectra.** It has been generally accepted for some years that spectra produced by atoms consist of series of lines, whereas those of molecules are made up of groups of bands. Molecular spectra can in general be divided into three types; the first, known as the "electronic band spectra," occurs in the ultra-violet or visible regions of the spectrum and may be studied in absorption, or else in emission under the stimulus of a suitable electrical discharge. The other two types, called "vibration-rotation" and "rotation" spectra, occur in the near and far infra-red, respectively; they are generally observed as absorption bands, although in some cases the corresponding emission bands can be studied at high temperatures. The theory of Bohr, as subsequently modified, has helped very considerably towards unravelling the complexity presented by the large number, often thousands, of lines observed in the spectra of atoms. In recent years a somewhat similar theory has been developed (*e.g.*, Kratzer, 1920) for molecules, and by means of it the intricacies of molecular, or band, spectra are being straightened out. The problem here is, however, much more difficult than with atomic, or line, spectra, for further analysis of the spectra of molecules, with instruments of high dispersive power, has shown the bands to consist of large numbers of individual lines, so close together as to give the impression of continuous absorption or emission of radiation. In spite of the difficulties, both of the experimental work and of interpreting the results obtained, the study of band spectra is already giving information of interest to the chemist; at present this information is restricted almost exclusively to simple compounds, but there is no doubt that in time the results of the analysis of molecular spectra will throw considerable light on



problems of the structure and dimensions of comparatively complex molecules.

### ENERGY LEVELS

**Quantisation of Energy.** In developing the theory of the spectra of molecules, in accordance with the principles used by Bohr for the study of atomic spectra, it is assumed that the energy of a molecule is not infinitely variable between certain limits, but that it can only have one of a definite set of values. In other words, the energy of a molecule is "quantised," and the molecule possesses only a limited number of energy levels; as with atoms, however, each main energy level has a number of subsidiary levels. The latter are not only responsible for the fine structure of the bands resulting from transitions between main levels, but transitions between sub-levels are the cause of the production of independent band systems. The main energy levels are called electronic levels, since it seems very probable that each corresponds with a slightly different electronic arrangement in the molecule. Under normal conditions the molecule is in its lowest energy level—the so-called "ground state"—but if it absorbs a sufficient amount of energy of the correct wavelength it may pass to a higher energy level with a somewhat different electronic configuration; the molecule is then said to be "activated" or "excited," and in this condition it is usually more chemically reactive than in the normal state. The energy difference between successive electronic levels varies with the nature of the substance, and of the particular levels considered, but a general idea of the magnitude may be obtained as follows.

**Electronic Levels.** The "critical potential" of a compound, that is the potential through which an electron must pass in order to acquire sufficient energy for it to suffer an inelastic collision with a molecule of the substance, is of the order of 1 to 10 volts. In the inelastic collision the electron is deprived of almost all of its energy, owing to the fact that its impact with a molecule causes a change in the electronic configuration of the latter; thus the transfer of energy from the electron to the molecule raises the energy level of the molecule. The energy difference between two



successive levels may thus be described as about 1—10 electron-volts or, as it is occasionally expressed, 1—10 volts; an average value may therefore be taken as 5 volts. This difference of energy can, for comparative purposes, be reduced to calories in the following manner: to convert electron-volts into ergs, it is necessary to multiply by  $4.774 \times 10^{-10}$ —the electronic charge—and to divide by 300; thus

$$1 \text{ electron-volt} \equiv 4.774 \times 10^{-10}/300 \text{ ergs} \quad . \quad . \quad . \quad (i.)$$

Dividing by the mechanical equivalent of heat,  $4.185 \times 10^7$  ergs  $\equiv$  1 calorie, gives the equivalent of the electron-volt in calories per *single molecule*; in order to obtain the value for 1 gm. mol. it is necessary to multiply by the Avogadro number  $6.062 \times 10^{23}$ , hence

$$1 \text{ electron-volt} \equiv 28,050 \text{ calories per gm. mol.} \quad . \quad . \quad (ii.)$$

The difference between two successive electronic energy levels is thus of the order of  $5 \times 28,000$ , *i.e.*, 115,000 calories per gm. molecule. This figure gives a general idea of the value of the energy change involved in an electronic transition, and indicates that molecules in the higher energy levels may be expected to be very active chemically. In connection with spectroscopic studies it is often convenient to know the energy difference in terms of ergs per single molecule; this may be readily found to be of the order of  $8 \times 10^{-12}$  ergs (equation (i.)) for 5 electron-volts.

**Radiation Frequency and Energy Changes.** According to the quantum theory of spectra, whenever a molecule gains, or loses, energy as a result of the transition from a lower to a higher energy level, or *vice versa*, the quantity of energy gained, or lost, is proportional to the frequency of vibration of the absorbed, or emitted, radiation. If  $E'$  represents the total energy of the molecule at the higher level, and  $E''$  that at the lower level, then

$$E' - E'' = h\nu$$

or 
$$\nu = \frac{E' - E''}{h} \quad . \quad . \quad . \quad . \quad . \quad (iii.)$$

where  $h$  is Planck's constant ( $6.547 \times 10^{-27}$  erg-secs.), and  $\nu$  is the radiation frequency in *vibrations per second*. As shown in the



previous paragraph, in an electronic transition  $E' - E''$  may be regarded as having an average value about  $8 \times 10^{-12}$  ergs, per molecule. The frequency of the radiation emitted, or absorbed, as a result of this transition is then given by

$$\begin{aligned}\nu &= 8 \times 10^{-12} / 6.547 \times 10^{-27} \\ &= 1.25 \times 10^{15} \text{ vibrations/sec.}\end{aligned}$$

Using the equation  $c = \nu\lambda$ , where  $c$  is the velocity of light ( $3 \times 10^{10}$  cm./sec.), and  $\lambda$  the wavelength of the radiation corresponding with the frequency  $\nu$ , it follows that the wavelength of the light emitted in the electronic transition under discussion is  $2.4 \times 10^{-5}$  cm., or 2400 Å (*i.e.*, Ångström units =  $10^{-8}$  cm.). Radiations of this wavelength come into the ultra-violet portion of the spectrum, and in fact the so-called electronic spectra of molecules are generally to be found either in the short wave region of the visible spectrum, or else in the ultra-violet.

**Energy Sub-levels.** Associated with each electronic level there are a number of sub-levels which account for the complex structure of the electronic bands of the molecule. In the first place it is supposed that the energy of vibration of the nuclei constituting the molecule can only have a limited number of possible values; that is, the vibrational energy is assumed to be quantised, and each energy value corresponds to a definite vibrational energy level. Each electronic level thus has a number of possible vibrational sub-levels, depending on the amplitude of vibration of the nuclei; the energy is greater the larger the amplitude. From a study of the structure of the electronic bands it appears that firstly, the energy differences between successive sub-levels is approximately one-tenth to one-hundredth part of the energy difference between successive electronic levels. Secondly, in each vibrational condition a molecule is supposed to have a number of possible energy states which depend on its speed of rotation about an axis passing through the centre of gravity. Hence every vibrational level has a set of rotational sub-levels, and the energy differences in successive levels of the latter are very roughly of the order of one-hundredth part that of successive vibrational levels of one and the same electronic state of the molecule.



The various energy levels may be represented diagrammatically in Fig. 10, in which  $A$  and  $B$  represent two of the main electronic levels of a molecule. Each of these has a series of vibrational sub-levels marked  $v = 0, 1, 2, 3, 4$ , etc., and for every one of the latter the possible rotational levels are designated by  $J = 0, 1, 2, 3, 4$ , etc.;  $v$  and  $J$  are called the vibrational and rotational quantum numbers, respectively, and it is in terms of these numbers that the corresponding energy values may be expressed. The energy difference between successive vibrational levels decreases as the quantum number  $v$  increases, but for successive rotational levels the energy change often increases slightly as  $J$  increases. When the molecule is in the lowest state  $A$  then it is in its normal condition, or "ground state," whereas for the electronic configuration represented by the  $B$  energy level the molecule is "activated" or "excited." The lowest possible energy level of the substance is represented by  $v = 0$ , and  $J = 0$ , in the state  $A$ .

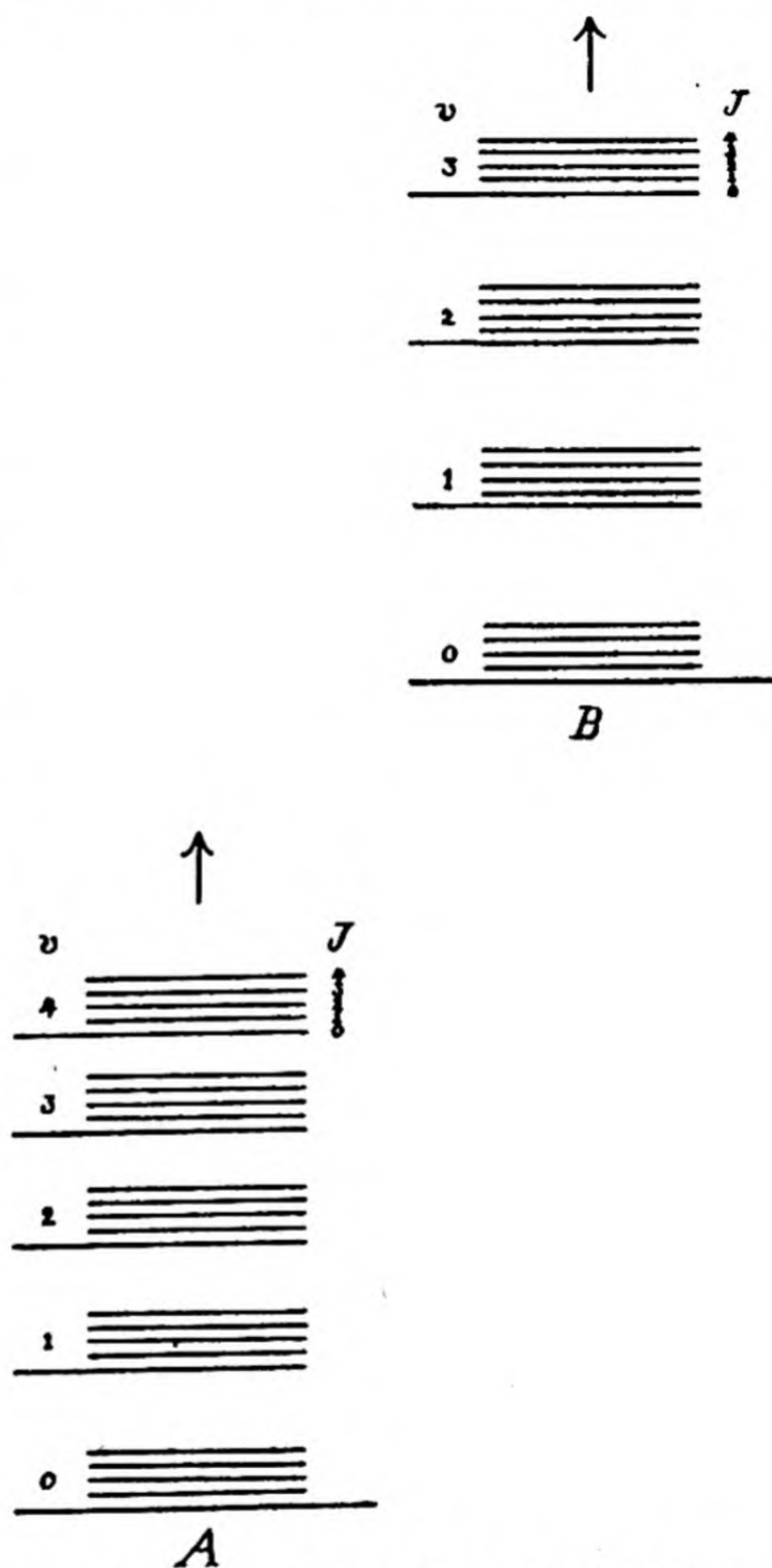


FIG. 10.—Diagrammatic representation of the energy levels of a molecule;  $A$  and  $B$  are two electronic states,  $v$  is the vibrational, and  $J$  the rotational, quantum number.

**Complexity of Spectra.** When a normal molecule in state  $A$  receives energy and becomes excited to the level represented by



*B* then, provided there is no change in the vibrational and rotational energy of the molecule, there should result, theoretically, an absorption spectrum consisting only of one line. Similarly other possible electronic changes would yield other single lines in the visible and ultra-violet regions of the spectrum. For any particular electronic change, however, the molecules are initially in various vibrational states and as a result of the transition find themselves in other vibrational states; the energy changes involved thus vary slightly for the individual molecules, so that the frequency of the absorbed radiation shows slight variations. Thus for every electronic transition there is a series of spectral lines corresponding to different vibrational energy transitions. Since the energy change between two successive vibrational levels is probably of the order of one-tenth of a volt, the variations in the energy of the electronic transition may be regarded as about one-fiftieth part of the total (5 volts). It can be readily shown that the separation between the successive fine structure lines in the electronic band spectrum situated at about  $2500\text{\AA}$  is thus roughly  $50\text{\AA}$ ; hence the vibrational lines for the same electronic transition are situated fairly closely together.

Simultaneously with the electronic and vibrational changes, rotational transitions may occur; for a definite electronic transition and a definite change in the vibrational energy each rotational transition will produce a line in the spectrum. Rotational energy changes are very small, and so these lines will be close together. A vibrational transition will, therefore, result in the production not of a single line but of a series of closely spaced lines, which under low spectroscopic resolution appear as a continuous absorption band. Every separate vibrational energy change results in the production of a separate band of this type: the whole set of bands for a given electronic transition being called a "band group" or "band system." Each electronic change occurring in the molecule will yield such a band system, and the whole series of band groups forms the complete electronic band spectrum of the particular substance. As a general rule each group of the electronic spectrum is produced separately depending on the conditions used for excitation.



The number of rotational and vibrational levels of a molecule is quite considerable ; hence the band spectrum should consist of a very large number of lines, closely spaced and even overlapping. In practice it is found, however, that only certain rotational transitions are possible, and this limits the number of lines ; the number is still large, but is not beyond the possibilities of analysis.

In considering the rotational energy of a molecule it must be remembered that rotation is possible about three axes ; for each type of rotation there is a set of energy levels and so the complete rotational spectrum is often very complex. For diatomic molecules the rotational energy about the axis joining the nuclei is zero, and the energies of the other two rotations are identical ; hence the

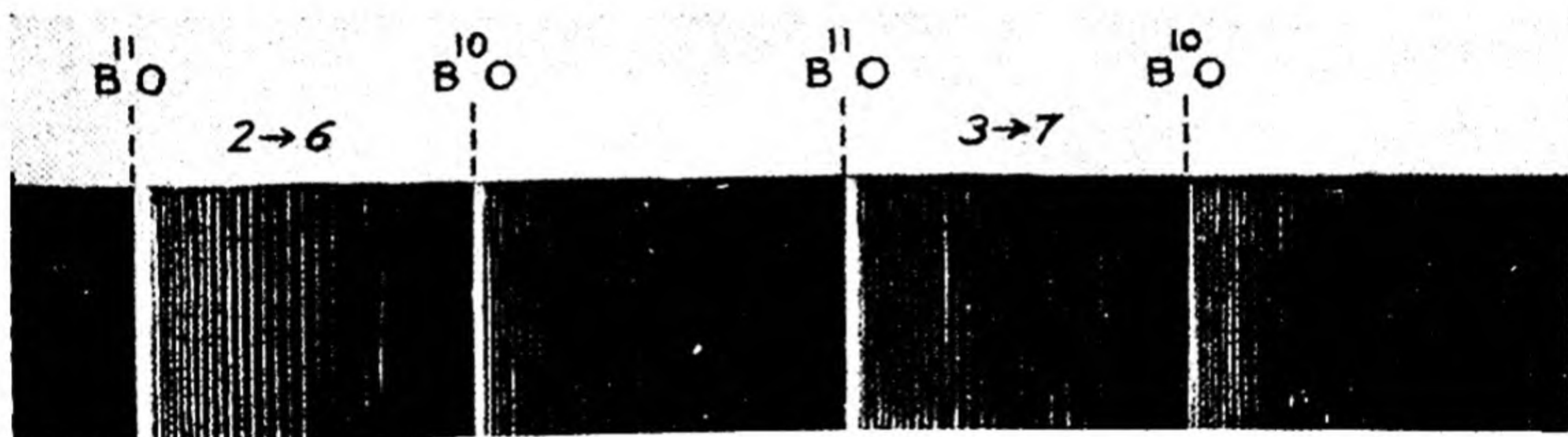


FIG. 11.—Enlarged portion of the  $\beta$  electronic band spectrum of the BO molecule ; each vibrational transition produces two bands on account of the existence of boron in two isotopic forms. The rotational fine structure of each band is clearly visible.

spectrum is comparatively simple. In other cases the rotation about two of the axes may be identical and the third different, *e.g.*, formaldehyde, but for complex molecules the three rotational energies are different, and the increase in the number of spectral lines makes interpretation of the band spectrum very difficult.

In Fig. 11 is seen a highly enlarged portion of the electronic band spectrum of BO, obtained as a result of the interaction of active nitrogen, containing a trace of oxygen, with boron trichloride ; the rotational fine structure of four vibrational bands is clearly visible.

**Vibrational Transitions.** Apart from the changes occurring during an electronic transition the vibrational energy level of the molecule may alter within one and the same electronic configuration. The transition from one vibrational level to another adjacent one would then result in an energy change of only about



one-tenth of a volt ; according to the method of calculation already given this transition would yield a spectral line with a frequency of approximately  $2.5 \times 10^{13}$  vibrations per sec., and hence a wavelength of  $1.2 \times 10^{-3}$  cm., *i.e.*,  $12\mu$ , or  $120,000\text{\AA}$ . The radiations due to vibrational changes only would thus appear in the near infra-red region of the spectrum, and in fact absorption spectra in this vicinity are invariably observed with heteropolar molecules, that is, with molecules possessing a permanent dipole (see Chapter III.); homopolar molecules, however, do not interact with radiation to undergo purely vibrational transitions. The spectra due to vibrational changes do not consist of single lines, since, as has been seen in connection with electronic changes, rotational transitions occurring simultaneously with that involving a vibrational energy change lead to the production of a number of very closely spaced lines. The resulting absorption spectrum appears, under low dispersion, as a continuous band in the near infra-red, but with high resolving power the individual lines due to the super-position of rotational energy changes on a particular vibrational transition may be distinguished. The absorption bands of this type generally occur within the wavelength region of 1 to  $23\mu$ , and are called "rotation-vibration" spectra. For each electronic configuration a number of vibrational transitions are possible ; this number is, however, limited by the fact that the transitions occur, as a general rule, from one level to the next, or to the next but one : that is,  $v$  changes by one or two, or possibly three, but rarely more.

A diatomic molecule has only one mode of vibration, but a more complex molecule has  $3n - 6$  vibrational modes, where  $n$  is the number of atoms in the molecule. Each type of vibration has its own set of energy levels and can give rise to its characteristic vibration-rotation spectrum. When there are a large number of atoms in the molecule the final result is apt to be complicated.

**Rotational Transitions.** The band spectra of molecules observed in the far infra-red, that is in the vicinity of wavelengths of  $200\mu$  or more, are apparently due to rotational transitions occurring whilst the molecule occupies a definite electronic level and a definite vibrational level. Such bands are called "rotational



spectra," and like the vibrational bands are produced only by heteropolar molecules. In order to account for the large wavelength, *i.e.*, small frequency, of the radiations involved in such transitions it is necessary to assume that the energy difference between two successive rotational levels is very small. This assumption is quite in harmony with the observed separations of the rotational lines both in the vibrational-rotational spectra and in the electronic bands.

Each possible rotational transition will produce a line in the rotational band, but the number of such lines is limited by the fact that  $J$  does not change by more than unity in each "jump." Owing to the close spacing the lines can only be observed with instruments of high resolving power. For a complex molecule, having several possible modes of vibration, the fine structure of the rotational bands, and also those of the vibrational-rotational spectra, will consist of a large number of lines.

In view of the great complexity of the spectra of molecules containing several atoms, most of the results capable of ready interpretation have been obtained with simple gaseous compounds. Until recently only the spectra of diatomic molecules had been given an unequivocal explanation, but progress is being made with more complex substances where the difficulty of sorting out into separate series the large number of rotational lines found in each spectral band often proves to be very great. As explained below, the lines in each series have an almost constant frequency separation, and this fact is made use of in the analysis of the fine structure of band spectra; if the lines are very close, however, and measurement, owing to experimental difficulties, not too accurate, different authors may propose different arrangements between which no decision is at present possible. The results described here will deal, therefore, more particularly with the conclusions of physico-chemical interest obtained from a study of the band spectra of simple gaseous molecules.

### ROTATIONAL SPECTRA

These spectra have been studied exclusively in absorption; homopolar molecules like oxygen, nitrogen, hydrogen and chlorine







which there is a transition from one level to the next ; that is, it is possible to simplify equation (v.) by putting  $J' - J'' = 1$ , and so

$$E'_J - E''_J = \frac{h^2}{8\pi^2 I} 2J' \quad . \quad . \quad . \quad . \quad . \quad . \quad (\text{vi.})$$

According to the quantum theory of spectra (see p. 185) this energy change may be equated to  $h\nu$ , where  $\nu$  is the frequency of the radiation resulting from the rotational transition; hence

$$\nu = \frac{h}{4\pi^2 I} m \quad . \quad . \quad . \quad . \quad . \quad . \quad (\text{vii.})$$

replacing  $J'$  by the general value  $m$ , which may have a series of integral values from unity onwards. (When  $m = 0$  there is, of course, no corresponding frequency.) The quantity  $h/4\pi^2 I$  is constant for a particular molecule, and so may be written as equal to  $b$ , that is

$$\nu = bm \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (\text{viii.})$$

The frequencies of the lines of the rotational spectrum should thus be :  $b, 2b, 3b, 4b$ , etc., and consecutive lines should have a constant frequency separation equal to  $b$ , *i.e.*,  $h/4\pi^2I$ . In actual practice Czerny found that the frequencies of the absorption maxima shown by the hydrogen halides in the far infra-red region of the spectrum were represented by the equation

$$v = bm - dm^3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (\text{ix.})$$

where  $d$  is a constant of the order of one ten-thousandth part of  $b$ . The frequency separation is thus not quite constant, but decreases very slightly as  $m$  increases ; this small deviation from constancy has been attributed to the fact that the molecule cannot be absolutely rigid, and so the moment of inertia does not remain constant, but increases during vigorous rotation.

**Molecular Constants.** From measurements on the infra-red absorption spectra the value of  $b$ , and hence of  $I$ , the moment of inertia at low rotational levels, may be determined. Some of the results obtained by Czerny are given in Table XLI.; these figures were slightly modified by the introduction of the equations of wave mechanics, but the values obtained are not very different from those given below.



TABLE XLI.—*Rotational Spectra of Hydrogen Halides*

Gas.	$b$ (cm. <sup>-1</sup> ).	$I$ (c.g.s.).	$r$ (cm.).
Hydrogen fluoride . .	41·14	$1·34 \times 10^{-40}$	$0·92 \times 10^{-8}$
Hydrogen chloride . .	20·83	2·66	1·28
Hydrogen bromide . .	16·70	3·31	1·42
Hydrogen iodide . .	12·84	4·31	1·62

It may be noted here that in spectroscopic work it is almost invariably the custom to express frequencies in terms of "wave-numbers," that is the number of vibrations *per cm.*, and they are written as  $\nu \text{ cm.}^{-1}$ . To convert the value of  $\nu$  in vibrations *per sec.*, as determined from the quantum theory equations, into wave-numbers, it is necessary to divide by  $3 \times 10^{10}$ , the velocity of light. The use of wave-numbers has the advantage over absolute frequencies in that the former are figures of normal magnitudes, whereas the latter involve large positive powers of ten, but it is somewhat unfortunate that the same symbol  $\nu$  is used to represent both. It is important to remember that the true frequencies must always be used in calculations. In Table XLI.,  $b$  is given in wave-numbers, but in order to determine  $I$  from the relationship  $b = h/4\pi^2 I$  these values should be multiplied by  $3 \times 10^{10}$ .

For a diatomic molecule of the type under discussion the moment of inertia about the axis perpendicular to the line joining the nuclei may be expressed in the form

$$I = Mr^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (\text{x.})$$

where  $r$  is the distance apart of the centres of gravity of the nuclei.  $M$  is the "reduced mass" of the molecule,\* defined by

$$\frac{1}{M} = \frac{1}{m_1} + \frac{1}{m_2} \quad \dots \dots \dots (xi.)$$

where  $m_1$  and  $m_2$  are the masses of the two nuclei; hence

\* The symbol  $\mu$  is frequently used for the reduced mass : it is not employed here so as to avoid confusion with the symbol for dipole moment and for the unit of length,  $10^{-4}$  cm.







**Isotope Effect.** The separation of consecutive lines in the rotational spectrum of a diatomic molecule depends on its moment of inertia, and this in turn is dependent on the masses of the atoms and their distance apart. In hydrogen chloride there are two types of molecule present: those in which the hydrogen is combined with the chlorine isotope of atomic weight 35, and those with the isotope of mass 37. If it may be assumed that the distance between the atoms is the same in each case, then the moments of inertia will be different, and consequently each of the two types of molecule will produce rotational spectra with different frequency separations; thus each line in the far infra-red spectrum should appear in duplicate. One line of each doublet, corresponding to the molecule containing the 35 isotope of chlorine, should be more distinct than the other, as the former is present in excess in normal chlorine. The difference in the separation of successive lines for the two kinds of hydrogen chloride molecule may be calculated as follows. Let  $I$  be the moment of inertia of one type of molecule, and  $I'$  the moment of the other type; if  $\Delta\nu$  is the frequency separation in the first case, and  $\Delta\nu'$  in the second, then it follows from equation (vii.) that

$$\Delta\nu = \frac{h}{4\pi^2 I} \quad \text{and} \quad \Delta\nu' = \frac{h}{4\pi^2 I'} \quad \dots \quad (\text{vii.}a)$$

and hence

$$\frac{\Delta\nu - \Delta\nu'}{\Delta\nu} = \frac{I' - I}{I'} \quad \dots \quad (\text{xiv.})$$

For the two forms of hydrogen chloride  $a_1$  and  $a_2$ , the atomic weights of the constituent atoms, are 1.008 and 35.00, and 1.008 and 37.00 respectively; inserting these values in equation (xiv.) it follows that

$$\frac{\Delta\nu - \Delta\nu'}{\Delta\nu} = \frac{1}{665}.$$

The average frequency separation for hydrogen chloride (Table XLI.) is about  $21 \text{ cm.}^{-1}$ , and so the "isotopic shift" ( $\Delta\nu - \Delta\nu'$ ) is approximately  $0.03 \text{ cm.}^{-1}$ ; owing to difficulties of studying spectra in the far infra-red this shift is probably too small to be detected. It may be concluded, therefore, that although rotational



bands should theoretically provide a means for the detection of isotopes, the line separations involved are too small to be capable of resolution. It will be shown below, however, that in vibrational-rotational spectra and in electronic band spectra definite indications of the presence of isotopes may be obtained, and in fact the spectroscopic method provides a means more sensitive in many cases than the mass spectrograph for detecting the presence of isotopes.

**Multiplicity of Rotational Levels.** The equation (iv.), in which  $J$  may have to be zero or integral, for the rotational energy of a rigid diatomic molecule is, strictly speaking, only applicable for a  $^1\Sigma$  state (p. 11). In other states the rotational quantum numbers may have different values, and in addition each rotational level may consist of a number of sub-levels with relatively small energy differences. The resultant rotational energy of a molecule depends in general on the relative extent of the magnetic interaction between the angular momentum of the nuclei of the molecule and the orbital and spin angular momenta along the internuclear axis,  $A$  and  $\Sigma$  respectively (see p. 11), of the electrons. Hund (1926) has distinguished four types of coupling of the angular momenta of the electrons: of these the two most common will be considered briefly.

**Case-a Coupling.** Case-a arises when there is a strong magnetic field associated with the orbital angular momentum along the internuclear axis ( $A$ ), so that it interacts strongly with the resultant spin vector  $S$ . This cannot take place unless both  $A$  and  $S$  are greater than zero, so that case-a is not possible for molecules in  $\Sigma$ -states ( $A = 0$ ), or for any molecule having a multiplicity of unity ( $S = 0$ ). When case-a does occur there are  $2S + 1$  electronic sub-levels to each electronic level, and associated with each there is a set of rotational levels, the energy of which is given by equation (iv.), with the condition that the lowest value of  $J$  is equal to  $A + \Sigma$  in each case, where  $\Sigma$  can have a number of values, viz.,  $S, S - 1, \dots, -S$ . An example of case-a coupling is found with nitric oxide in its ground state:  $A$  is equal to 1 and  $S$  is  $\frac{1}{2}$ , so that it is described as a  $^2\Pi$  level. The possible values of  $\Sigma$  are  $+\frac{1}{2}$  and  $-\frac{1}{2}$ , hence  $\Sigma + A$  can be  $\frac{1}{2}$  or  $\frac{3}{2}$ , and the two electronic sub-levels, which have an appreciable



energy difference, are described as  ${}^2\Pi_{\frac{1}{2}}$  and  ${}^2\Pi_{\frac{3}{2}}$ , respectively: the subscripts determine the minimum values of  $J$  for the two levels, which are accordingly  $\frac{1}{2}$ ,  $\frac{3}{2}$ ,  $\frac{5}{2}$ , . . . etc., for the former, and  $\frac{3}{2}$ ,  $\frac{5}{2}$ ,  $\frac{7}{2}$ , . . . etc., for the latter.

**Case-b Coupling.** When the interaction between  $L$  and  $S$  is relatively small, then coupling may be of the case-b type: this always arises in  $\Sigma$  states, except  ${}^1\Sigma$ , and it may occur in other states. The multiplicity of rotational levels in case-b is generally referred to as "spin splitting." The component levels arising from  $S$  being greater than zero are designated  $F_1$ ,  $F_2$ ,  $F_3$ , etc., according as the rotational quantum number  $J$  has values  $K + S$ ,  $K + S - 1$ , . . .,  $K - S$ , respectively, where  $K$  can have a series of integral values commencing with  $L$ . The molecule of oxygen exhibits case-b coupling: it has a  ${}^3\Sigma$  term in its ground state, and  $L$  and  $S$  are both equal to unity. The three components of this electronic level are  $F_1$ ,  $F_2$  and  $F_3$ , and the lowest values of  $J$  are  $K + 1$ ,  $K$  and  $K - 1$ , respectively, where  $K$  has integral values commencing with 1, since  $L$  is unity in this case. It may be noted that on account of the symmetry of the  ${}^{16}\text{O}^{16}\text{O}$  molecule only alternate rotational levels with odd values of  $K$  are possible (see "Recent Advances in General Chemistry," Chapter III.). In general alternate rotational levels are missing when a diatomic molecule has two identical nuclei without spin.

**$L$ -type Doubling.** In addition to the multiplicity arising from magnetic interaction there is a doubling of rotational levels which occurs in all except  $\Sigma$  states: this is known as  $L$ -type doubling, the separation between the rotational doublets being relatively small. The doubling occurs for each rotational state, so that with nitric oxide, for example, every rotational level is virtually composed of four sub-levels.

The multiplicity of rotational levels brings about considerable complexity, especially in the electronic spectra of diatomic molecules; although it is of little importance in connection with purely rotational spectra the subject is considered here for the sake of completeness, as references to the various types of coupling and the multiplicities of levels are frequently mentioned in the literature ("Recent Advances in General Chemistry," Chapter II.).



# VIBRATIONAL-ROTATIONAL SPECTRA

These spectra, which are found in the near infra-red, are also studied in absorption ; like the pure rotational spectra they are not obtained normally for homopolar molecules, but only with those possessing an electric moment. The experimental technique in the near infra-red is not so difficult as that for the longer wavelength region of the spectrum ; in the first place recent improvements in experimental methods have made high resolution possible, and by the use of specially sensitised plates infra-red absorption spectra have been studied photographically up to wavelengths of 1 to  $2\mu$ . Vibrational-rotational spectra of a number of gaseous molecules of varying complexity have already been studied, and the bands resolved into their constituent lines ; the interpretation of the many lines obtained is, however, not always possible. As already indicated the near infra-red spectrum of a molecule consists of a number of bands ; every band corresponds to a transition from one vibrational level to another, and the fine structure of each is due to rotational changes occurring at the same time.

**Vibrational Energy of a Diatomic Molecule.** According to the newer developments of the quantum theory the vibrational energy ( $E_v$ ) of a harmonic oscillator is given by the expression

$$E_v = (v + \frac{1}{2})h\omega_e \quad . \quad . \quad . \quad . \quad . \quad . \quad (xv.)$$

where  $v$  is the vibrational quantum number, which may be equal to zero or an integer, and  $\omega_e$  is the equilibrium frequency of vibration of the oscillator. This quantity is the hypothetical vibration frequency of the molecule for vibrations of zero amplitude about the equilibrium positions of the nuclei. The frequency  $\omega_e$  is generally stated in "wave-numbers," which is obtained by dividing the value from equation (xv.) by  $3 \times 10^{10}$ , the velocity of light. For the sake of simplicity the latter factor is omitted from all equations, although it should be included when calculations are made in terms of wave-numbers. The total vibrational and rotational energy (see equation (iv.)) of a diatomic molecule, assuming no interaction between the two types of energy, should thus be



$$E = (v + \frac{1}{2})h\omega_e + \frac{h^2}{8\pi^2I} J(J + 1) \quad . \quad . \quad . \quad (xvi.)$$

Assuming, for the present, the rotational energy to remain unaltered, and that the vibrational quantum number changes by unity, the energy change in the transition would be

$$E' - E'' = h\omega_e \quad . \quad . \quad . \quad . \quad . \quad (xvii.)$$

and the corresponding spectral frequency, according to the quantum theory, would be equal to  $\omega_e$ : this would represent the "origin" of the vibrational-rotational band.

**Anharmonic Vibrations.** If the change in vibrational level is restricted to unity at every transition, as would be the case for a truly harmonic oscillator, each mode of oscillation in the molecule should produce one vibrational-rotational band only; analysis of the structure would then be comparatively simple, and information could readily be obtained concerning the symmetry of the molecule. In actual fact, however, the nuclear vibrations are anharmonic and the change in the vibrational quantum number is sometimes two and three, as well as unity. When  $v' - v'' = 1$  the band produced is called the "fundamental," and the others, at frequencies approximately two and three times that of the fundamental, are called "overtones" or "harmonics." In addition vibrational spectra frequently result from the combination of two modes of oscillation; the presence of such bands complicates the infra-red spectrum and makes a definite interpretation of the results difficult. For example, thirteen bands have been observed in the near infra-red spectrum of ammonia gas, but it is probable that these are made up of three fundamental frequencies, together with their overtones and combination frequencies. The overtone frequencies are not exact multiples of that of the fundamental, because the energy of an anharmonic oscillator is not quite the same as given in equation (xv.) for harmonic vibrations; in the former case, the first two terms of the equation for vibrational energy may be represented by

$$E_v = (v + \frac{1}{2})h\omega_e - (v + \frac{1}{2})^2 x h\omega_e \quad . \quad . \quad . \quad (xviii.)$$

where  $x$ , the "anharmonicity constant" of the oscillator, repre-



sents the departure from harmonic motion. Neglecting for a moment the rotation of the molecule, if a change occurs from a vibrational level of quantum number  $v = n$  to the level for which  $v$  is zero, the frequency of the radiation emitted will be given by

$$\nu = n\omega_g[1 - (n + 1)x] \quad . \quad . \quad . \quad . \quad (\text{xix.})$$

The value of  $\nu$  gives the position of the origin of the band, and for values of  $n$  equal to 1, 2 and 3, respectively, the corresponding frequencies are

$$\nu_1 = \omega_e(1 - 2x)$$

$$\nu_2 = 2\omega_e(1 - 3x)$$

and

$$\nu_3 = 3\omega_e(1 - 4x).$$

The frequency  $\nu_1$  represents that of the origin of the fundamental band, and  $\nu_2$  and  $\nu_3$  are the frequencies for the first two harmonics. It is clear from the equations that  $\nu_2$  is not exactly equal to  $2\nu_1$ , nor is  $\nu_3$  equal to  $3\nu_1$ , but the agreement is approximate if  $x$  is small. Since the wavelength is proportional to the reciprocal of the frequency, the wavelength of the fundamental band will not be an exact multiple of the values for the overtones, although it will be approximately so. For example, hydrogen chloride has a fundamental at  $3.46\mu$ , and so the first and second overtones should be found close to  $1.73$  (*i.e.*,  $3.46/2$ ) $\mu$ , and  $1.15$  (*i.e.*,  $3.46/3$ ) $\mu$ , respectively; the actual wavelengths of these overtones, or harmonics, have been found to be  $1.76\mu$  and  $1.19\mu$ . Similar results have been obtained with carbon monoxide, which has a fundamental at  $4.67\mu$ , and harmonics at  $2.35\mu$  and  $1.57\mu$ .

**P and R Branches.** If the effects of anharmonicity and of interaction are neglected the sum of the vibrational and rotational energies may be represented by equation (xvi.), and the energy change  $E' - E''$  for a simultaneous transition from the vibrational level  $v'$  to  $v''$ , and rotational level  $J'$  to  $J''$ , would be given by

$$E' - E'' = h\omega_e(v' - v'') +$$

$$\frac{h^2}{8\pi^2 I} [J'(J' + 1) - J''(J'' + 1)] \quad . \quad . \quad . \quad (\text{xx.})$$

For the *fundamental* band  $v' - v''$  is equal to unity, and the change in the rotational quantum number is always restricted







spectrum of hydrogen chloride in the near infra-red has given results in conformity with these views; the series of maxima occurring in the fundamental band at  $3.46\mu$  is shown in Fig. 12. At the centre of the band there is obviously a missing line, and the corresponding frequency, calculated from the values for the lines on each side of the gap, gives the equilibrium frequency of vibration ( $\omega_e$ ) of the oscillator. It will also be observed from Fig. 12 that the intensity of absorption decreases as the value of  $m$ , whether positive or negative, increases.

**Q branch.** For a molecule possessing angular momentum about the axis joining the nuclei, the vibrational transition is possible

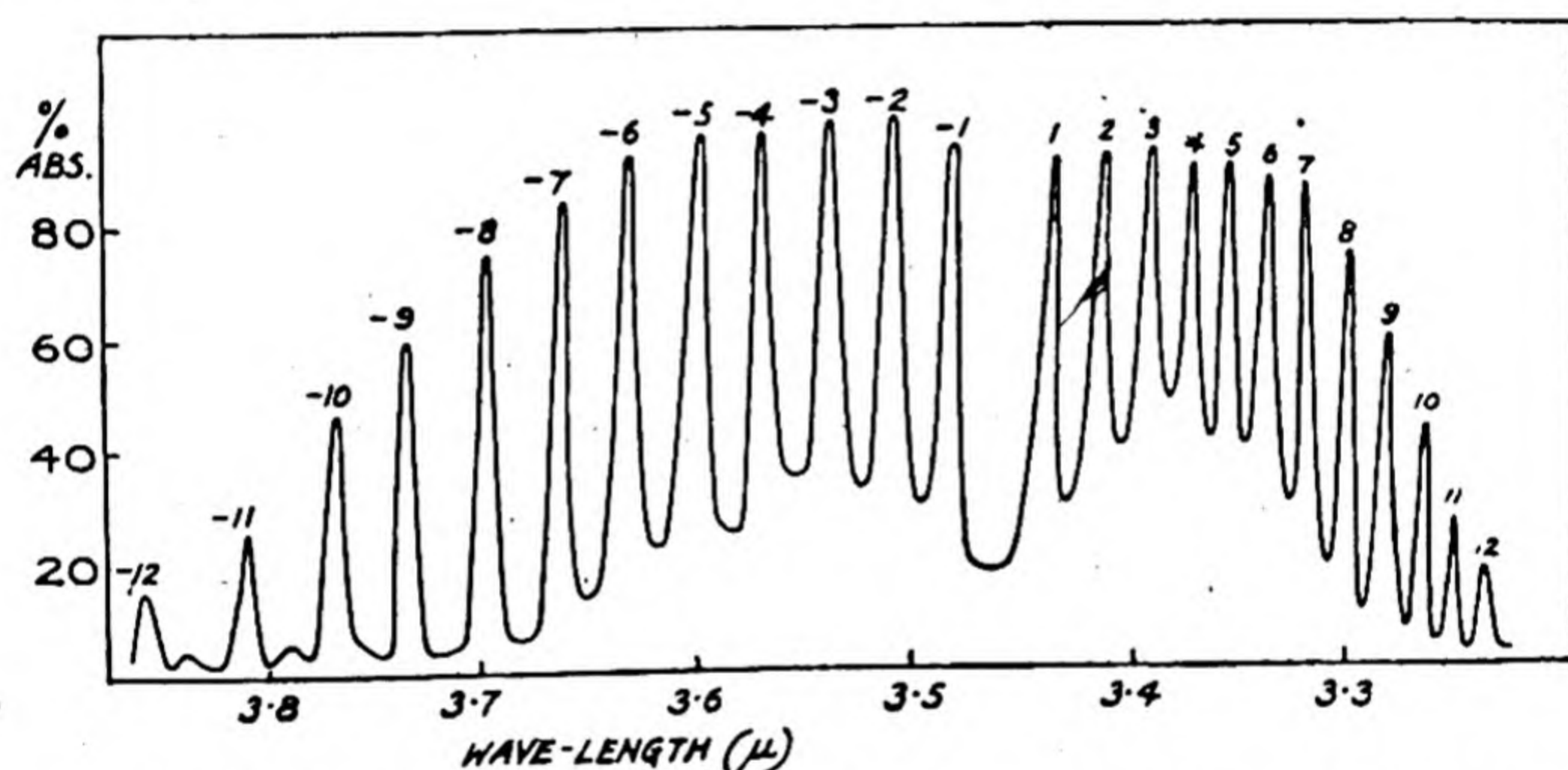


FIG. 12.—The fundamental vibration-rotation band of hydrogen chloride at  $3.46\mu$ . (After Imes.)

in which there is no change in the rotational quantum number; in such cases a so-called **Q branch** is formed at the centre of the band. It might appear, at first sight, from equation (xxii.) that the **Q branch** should consist of a single line for each vibrational change; actually it often has a definite fine structure. This may be accounted for by taking into consideration the fact that the moment of inertia of the molecule is not necessarily the same at the initial and final stages of the vibrational transition; if these are  $I'$  and  $I''$ , respectively, the energy of the vibrating-rotator, according to equation (xvi.) will be:

$$E' = (v' + \frac{1}{2})h\omega_e + \frac{h^2}{8\pi^2 I'} J(J + 1) \quad . \quad . \quad (xvi.a)$$



and 
$$E'' = (v'' + \frac{1}{2})h\omega_e + \frac{h^2}{8\pi^2 I''} J(J+1) \quad . \quad . \quad (\text{xvi.b})$$

assuming no change in the rotational quantum number. If  $v' - v''$  is equal to unity, for the fundamental band, then

$$E' - E'' = h\omega_e + \frac{J(J+1)h^2}{8\pi^2} \left( \frac{1}{I'} - \frac{1}{I''} \right) \quad . \quad (\text{xxiii.})$$

and, therefore, 
$$\nu_Q = \omega_e + \frac{J(J+1)h}{8\pi^2} \left( \frac{1}{I'} - \frac{1}{I''} \right) \quad . \quad . \quad (\text{xxiv.})$$

The difference between  $I'$  and  $I''$  has the effect of making the second term on the right-hand side different from zero, and a series of lines in the  $Q$  branch, all fairly close together, will be obtained for different values of  $J$ .

The  $Q$  branches are frequently observed with polyatomic molecules, *e.g.*, ammonia, but there is only one case on record in which a diatomic molecule shows this type of spectrum in the near infra-red. It is well known that nitric oxide is one of the few compounds with an odd number of electrons (see p. 69), and as a result the molecule does not rotate in one plane as do other diatomic molecules. There is thus an angular momentum resulting in the formation of a  $Q$  branch in the vibration-rotation band observed at a wavelength of about  $5.30\mu$  (Snow, Rawlins and Rideal, 1929).

**Frequency Separation of Rotational Lines.** In general, apart from the centre of the band, the frequency separation  $\Delta\nu$  of two successive rotational lines in the vibration spectrum is, according to equation (xix.), equal to  $h/4\pi^2 I$ ; hence from a study of the near infra-red bands it is possible to calculate the moment of inertia of a molecule, and the value should, of course, be the same as that determined from the purely rotational spectrum (p. 195). The measurements in the former case are, however, much easier to carry out. For hydrogen chloride Imes (1920) found that the average separation of two consecutive lines in the band with centre at  $3.46\mu$  was  $20.9 \text{ cm.}^{-1}$ ; hence the moment of inertia of the molecule can be calculated to be  $2.64 \times 10^{-40}$ , in comparison with the value of  $2.66 \times 10^{-40}$  c.g.s. units obtained from the observations of Czerny on the pure rotation spectrum (p. 194).



The separation of the lines should be independent of the nature of the band, that is whether it is the fundamental or an overtone, apart from the variations due to small changes in the moment of inertia of the molecule; the mean value of the latter, and hence the distance apart of the centres of the nuclei, may be determined by an examination of any of these bands. Each successive overtone brings the band nearer the visible portion of the spectrum, *i.e.*, higher frequency region, and consequently becomes more susceptible of investigation by accurate photographic methods; in this way it is often possible to get more reliable values for the frequency separation of the rotational fine structure lines. Unfortunately the absorption intensity generally decreases with increasing frequency of the overtone, and so there is a limit to the extent of the observations which can be made in this manner.

As in the case of pure rotation bands the distance apart of successive lines in the vibration-rotation spectrum is not quite constant; this is not only due to changes in the moment of inertia, but also to some kind of interaction between vibrational and rotational movements. In calculating the frequency of the absorbed radiation (p. 200) it was assumed that the rotational and vibrational energies could be added to one another algebraically, but if this is not exactly true the frequencies will deviate somewhat from the calculated values. The rotational lines, as a rule, become slightly further apart on one side of the centre of the band, and crowd together somewhat on the other side. With hydrogen chloride the crowding occurs on the side of increasing frequency, that is in the *R* branch, but it is not necessarily so for all molecules.

**The Restoring Force in Hydrogen Halide Molecules.** From an examination of the vibration-rotation and the rotation spectra of three hydrogen halides Czerny (1928) observed that the quantity  $\omega_e^2/b$ , where  $\omega_e$  is the fundamental vibration frequency of the molecule, and  $b$  is equal to  $h/4\pi^2I$ , was almost constant for the compounds studied. The appropriate results, including those for hydrogen iodide (Nielsen, 1935), are given in Table XLIII.







### TABLE XLIV

### Relative Restoring Forces between the Nuclei in Hydrogen Halides

Gas.	Relative Force.
Hydrogen fluoride . . . .	3·08
Hydrogen chloride . . . .	1·59
Hydrogen bromide . . . .	1·30
Hydrogen iodide. . . .	1·00

These figures account readily for the fact that hydrogen iodide dissociates most easily on heating.

## ISOTOPE EFFECT

The presence of molecules containing atoms in two different isotopic forms will have the same effect on the frequency separation of the rotational fine structure lines in the vibration spectrum as in the pure rotation spectrum. For hydrogen chloride it has been shown that the difference for two isotopic molecules is less than one six-hundredth part of the normal frequency separation between successive lines; this variation is probably much too small to have any influence on the measurements possible at the present day. There is, however, another factor related to the mass of the nuclei constituting the molecule that has a much larger effect on the vibration-rotation spectrum. It has been stated already that

$$2\pi\omega_e = \sqrt{f/M} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (\text{xxv.})$$

hence

$$\omega_e \propto \sqrt{f/M}$$

if the oscillation of the nuclei is assumed to be harmonic. If the binding force for a given molecule, *e.g.*, hydrogen chloride, is independent of the particular isotope present, then  $f$  may be taken as a constant, and

$$\omega_e \propto \sqrt{1/M}.$$

Consider two molecules each containing a different isotope : suppose the corresponding reduced masses are  $M$  and  $M'$ , and the equilibrium vibration frequencies are  $\omega_e$  and  $\omega_e'$ , then







equal to  $\lambda$  for either isotope since they are not very different, corresponds to a wavelength of about  $3.46\mu$  (p. 201). Hence the "isotopic shift" at the centre of the band should be  $3.46 \times 0.00077\mu = 26.64\text{\AA}$ , and in accordance with the views already outlined each rotational line should consist of a doublet with its constituents  $26.6\text{\AA}$  apart. In the case under discussion  $M'$  refers to the heavier isotope, and so  $\delta\nu$  is positive and  $\delta\lambda$  negative; that is the wavelengths of the lines due to the heavier isotope are greater than those due to the lighter isotope. Since the latter is present in excess in ordinary chlorine, and also hydrogen chloride, the shorter wavelength (*i.e.*, higher frequency) component of each

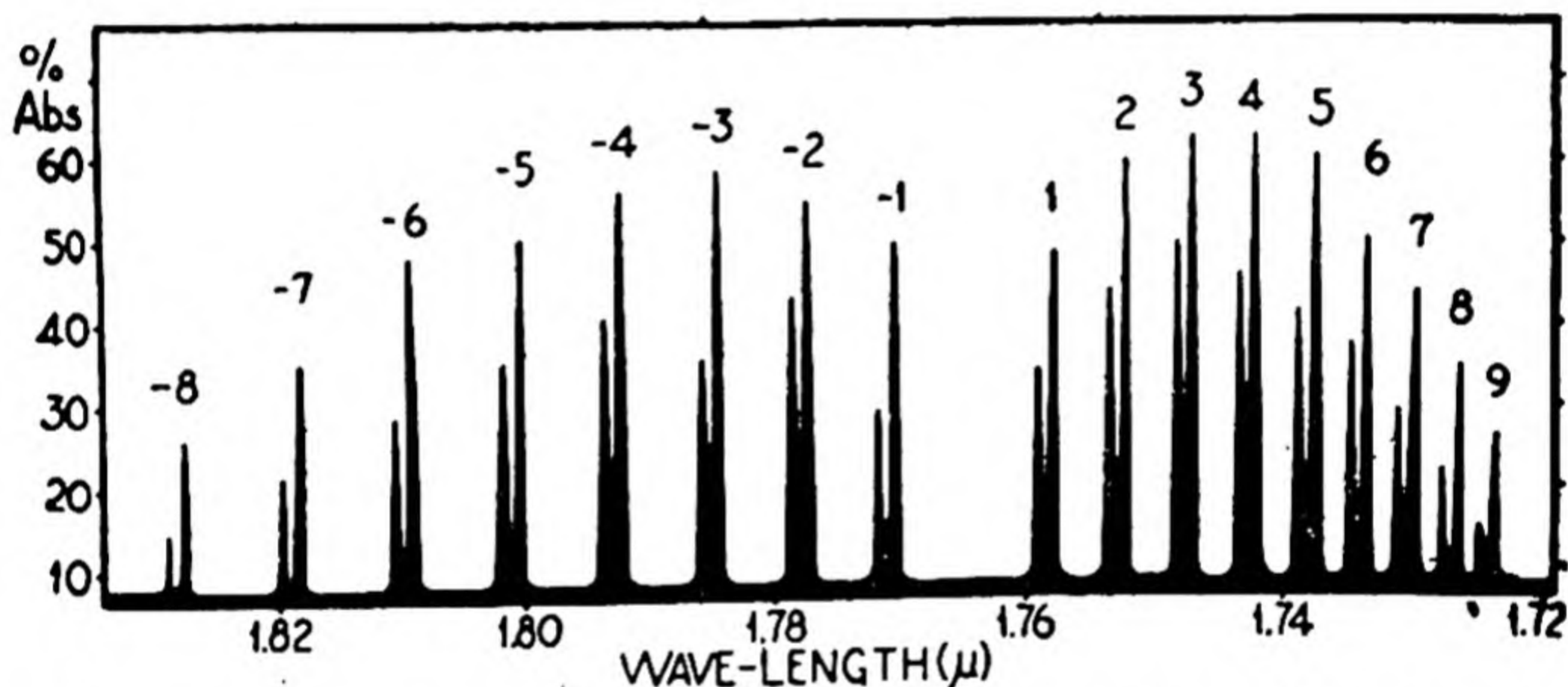


FIG. 13.—The first harmonic band in the vibrational-rotational spectrum of hydrogen chloride; each rotational line appears as a doublet resulting from the existence of chlorine in two isotopic forms. (After Meyer and Levin.)

rotational doublet should be stronger than the longer wave (lower frequency) component. By the use of high dispersion apparatus Randall and Imes (1920), and later Meyer and Levin (1929), showed that the rotational lines in the infra-red vibration spectrum of hydrogen chloride were doublets (Fig. 13) with the relative intensities in favour of the higher frequency component corresponding with the lighter isotopic molecule. The separation between the lines of each doublet was found to have a mean value of about  $25 \pm 2\text{\AA}$  in comparison with the calculated value of  $26.6\text{\AA}$ .

Since the frequencies of the origins of overtone bands are approximately equal to  $n\nu$ , the values for two isotopic molecules would be  $n\nu$  and  $n\nu'$ , respectively, and the separation between



them  $n(\nu - \nu')$  is equal to  $n\delta\nu$ , where  $\delta\nu$  is the separation in the fundamental band. The corresponding wavelength separation would be  $\delta\lambda/n$ : the term  $\delta\lambda$  having the value determined for the fundamental band. For the first harmonic of hydrogen chloride ( $\lambda = 1.76\mu$ ),  $n$  is equal to 2, and so the wavelength shift for the isotopic forms of chlorine would be  $26.64/2 = 13.32\text{\AA}$ ; all the rotational lines in this particular band should, therefore, be doublets with a separation of  $13.3\text{\AA}$ . In the detailed study of the  $1.76\mu$  band Imes (1919) found the separation to be  $14 \pm 1\text{\AA}$ : the agreement with the calculated value is excellent. If more accurate values of the isotopic shift are to be calculated, or if the accurate determination of the isotopic shift is to be used—as it may well be—to calculate the relative atomic weights of isotopes, allowance must be made for the fact that the oscillations of the nuclei are not truly harmonic.

The discovery of the hydrogen isotope of mass 2 (deuterium) has been followed by a search for the infra-red band of the corresponding hydrogen chloride molecule  $^2\text{HCl}$ ; this has been found by Hardy, Barker and Dennison (1932) with its origin at  $4.8\mu$ . Lines for both  $^2\text{H}^{35}\text{Cl}$  and  $^2\text{H}^{37}\text{Cl}$  have been distinctly observed. Since the atomic weight of the hydrogen is double that in ordinary hydrogen chloride the equilibrium vibration frequency ( $2091\text{ cm.}^{-1}$ ) is less than the normal value ( $2939\text{ cm.}^{-1}$ ) and consequently the vibration band is situated at longer wavelengths.

In the present chapter the doubling of the fine structure in vibration bands has so far only been used to confirm the existence of the isotope effect where the presence of isotopes is definitely known to occur. It will be shown later, however, that the same effect in the electronic bands of molecules has indicated the existence of isotopes of carbon, nitrogen and oxygen which had not been detected by observations with the mass spectrograph.

## ELECTRONIC BANDS

As already indicated, the bands due to electronic transitions appear in the ultra-violet or visible portions of the spectrum; these bands have been studied both in absorption and emission.



All types of molecules, whether homopolar or heteropolar, yield electronic bands, and the fine structure due to vibrational and rotational changes is observed in many cases; the conditions under which the structure disappears will be discussed in subsequent sections. From measurements on the electronic band spectrum it is thus possible to calculate the moments of inertia, and hence the distances between the nuclei in homopolar, as well as in heteropolar, molecules; information has also been obtained in this manner concerning the isotopes of homopolar molecules.

**Complexity of Electronic Bands.** Although the technique for studying bands in the ultra-violet and visible portions of the spectrum is much simpler than that for measurement in the



FIG. 14.—A portion of the  $\beta$  system of the band spectrum due to the BO molecule; the figures below the photograph indicate the initial and final vibrational quantum numbers. Each vibrational band appears in duplicate, indicated by full and dotted lines, because of the isotopic forms of boron. The rotational fine structure can be detected in some of the bands.

infra-red region, the electronic bands are often so complex as to render their elucidation extremely difficult. Whereas changes in vibrational levels in the infra-red are limited to one, two or three at the most, in the course of an electronic transition the energy changes are so comparatively large (p. 184) that the vibrational quantum number often alters by ten or more. For every electronic transition there is a band group, made up of a number of bands, each corresponding to a particular vibrational change; every one of these bands consists of a number of lines due to rotational transitions. From what has been said concerning the multiplicity of rotational levels (p. 197), it is evident that the number of rotational lines may be very large. For symmetrical molecules, the nuclei of which possess no spin momentum, alternate rotational



levels are missing, but for others, *e.g.*, hydrogen, deuterium, nitrogen, chlorine and acetylene, the atoms of which have nuclear spin, there is a definite alternation in the intensity of successive lines ("Recent Advances in General Chemistry," Chapter III.).

Since each type of oscillation possible in the molecule will produce its own set of vibrational bands, and each kind of rotation its fine structure, the complexity may be very great (see Fig. 14). As a rule the number of different electronic levels of a molecule is quite large, and several transitions are possible, each of which yields a separate band group; if these groups overlap the elucidation of the spectra is further complicated. Generally, however, different methods of excitation may be used to produce different groups of bands in the emission spectrum.

**Analysis of Bands.** Examination of a band group shows that in general each vibrational band is sharply defined at one end—the so-called "head" of the band—and more diffuse at the other; the band is said to be "degraded" in the diffuse direction. The head of the band has no special theoretical significance; it is well marked because, as will shortly appear, the rotational lines are crowded together in its vicinity, whereas they are spaced further apart towards the degraded end of the band. The centre, or origin, of each vibrational band is sometimes marked by a gap as in the vibrational-rotational spectrum, but generally a *Q* branch (p. 203) is possible, even with diatomic molecules, and then the origin of the band is not so easily found.

If the vibrational and rotational energy changes are simply added algebraically to the electronic energy change, the frequency of any line resulting from a given electronic transition would be given, approximately, by

$$\nu = \nu_e + (v' + \frac{1}{2})\omega_e' - (v'' + \frac{1}{2})\omega_e'' + hm/4\pi^2I \quad . \quad (\text{xxxi.})$$

where the electronic energy change is equal to  $h\nu_e$ ,  $v'$  and  $v''$  are the vibrational quantum numbers, and  $\omega_e'$  and  $\omega_e''$  the equilibrium vibration frequencies of the molecule in the upper and lower electronic states. This equation involves two assumptions in particular: firstly, the oscillations of the molecule are assumed to be harmonic, and secondly, no allowance is made for the differ-



ence of the moment of inertia in the two states of the molecule. For an accurate analysis of the electronic bands it is necessary to make allowance for this difference, but in the approximate equation given here it is assumed that  $I$  has a mean value between that of the initial and final electronic states; this is close enough for present purposes.

**The Cause of the Band Head.** For a given electronic transition and a given vibrational change, the quantity  $\nu_e + (v' + \frac{1}{2})\omega_e' - (v'' + \frac{1}{2})\omega_e''$  represents the frequency of the origin of the particular vibrational band produced in the transition under discussion; this is, of course, a constant for the given band, and may be represented by the symbol  $\nu_0$ . The equation for the frequency of any line in this band can then be written in the form

$$\nu = \nu_0 + bm + cm^2 \quad \dots \quad (xxxii.)$$

where  $m$  has integral values, and possibly zero, and  $b$  and  $c$  are constants. The term  $b$  is equal to  $h/4\pi^2I$ , the moment of inertia  $I$  being that in the lower electronic state, and  $c$  is a factor, of the order of one-tenth of  $b$ , or less, which corrects for changes in the moment of inertia in the different electronic configurations. The constant  $c$  may be positive or negative according to the nature of the molecule. If  $c$  is negative then as  $m$  increases in the series  $+1, +2, +3$ , etc. (*R* branch), the value of  $\nu$  at first increases: as  $cm^2$  is growing at a more rapid rate than  $bm$ , however, the frequency spacing between successive lines gradually decreases, and the lines begin to crowd together. At a certain value of  $m$  the term  $cm^2$  exceeds  $bm$  numerically, and the frequencies of successive lines now commence to form a decreasing series with spacings becoming steadily greater. In the vicinity of the point at which the reversal occurs it is clear that the rotational lines of the band will crowd together, and there will generally be a sharp boundary where the lines cease to proceed in one direction, and commence to go in the reverse way with increasing values of  $m$  (see Figs. 11 and 14). This sharp limit represents the "head" of the band, and its position, with respect to the origin, depends only on the ratio of  $b$  to  $c$ .

For the case under consideration, with  $c$  negative, it is clear



that the head of the band will occur on the higher frequency side : that is towards the violet end of the spectrum. In the same band there will also be a series of lines for which  $m$  has the values  $-1, -2, -3$ , etc. ( $P$  branch) ; from equation (xxxii.) it may be seen that these lines will gradually decrease in frequency, if  $c$  is negative, and the separation of consecutive lines will become larger as  $m$  increases numerically. At the same time, as is the case in all band spectra, the intensity of the lines diminishes, so that the band shades off on the lower frequency side ; such a band is said to be degraded towards the red end of the spectrum. For electronic transitions with molecules having a positive value of  $c$ , the lines will spread out in the  $R$  branch and hence degrade towards the short-wave end ; the head of the band will then appear in the  $P$  branch at the red end of the spectrum. From this discussion it will be seen that although the head of a band has no theoretical significance it does help in the identification of a band, and measurement of the frequency of band heads is often useful, when a number of band groups overlap, in sorting out the series belonging to each electronic transition.

It should be noted in passing that a band head should, theoretically, appear in ordinary vibration and rotation spectra ; in these cases, however, the moment of inertia does not change very markedly as a result of energy transitions, and the deviation factor  $d$  (equation (ix.), p. 193) is small. The head of a band would only appear at large values of  $m$ , but the intensity of the lines is then so feeble as to render them, and consequently the band head, undetectable.

**Moments of Inertia from Electronic Bands.** If one of the states of the molecule taking part in an electronic transition is the normal unexcited state then the constant  $b$  may be put equal to  $h/4\pi^2 I$ , where  $I$  is the normal moment of inertia. By sorting out the rotational lines of a band into the  $P$ ,  $Q$  and  $R$  branches—not always an easy matter—it is possible to determine the value of  $b$ , using equation (xxxii.), and hence to calculate  $I$  and also  $r$ , the mean distance apart of the nuclei (p. 195). The results obtained should, of course, be the same as those determined—wherever possible—from the infra-red spectra. Thus, for nitric oxide the



value of  $I$  calculated from observations on electronic band spectra is  $16.3 \times 10^{-40}$  c.g.s. units ( $r = 1.15 \times 10^{-8}$  cm.), whereas the examination of the vibrational-rotational bands gives  $I$  as  $16.4 \times 10^{-40}$  c.g.s. units ( $r = 1.15 \times 10^{-8}$  cm.). For a homopolar molecule there is no infra-red spectrum, and so molecular dimensions can be calculated from spectroscopic measurements if the electronic bands have been analysed.

**Anharmonic Vibrations.** It has been already indicated that in an electronic transition the frequency ( $\nu_0$ ) of the origin of any particular band may be represented by the equation

$$\nu_0 = \nu_e + (v' + \frac{1}{2})\omega_e' - (v'' + \frac{1}{2})\omega_e'' \quad . \quad . \quad . \quad (\text{xxxiii.})$$

if  $\omega_e'$  and  $\omega_e''$  are the equilibrium vibration frequencies of the molecules in upper and lower states of the electronic transition, and  $v'$  and  $v''$  are the corresponding vibrational quantum numbers. This equation only holds exactly if the oscillations are truly harmonic, and in order to represent the actual frequencies it is generally necessary to include terms involving  $(v + \frac{1}{2})^2$ , and possibly  $(v + \frac{1}{2})^3$ , as well as the anharmonic constants (see p. 200); thus taking the squared term only into consideration

$$\nu_0 = \nu_e + [\omega_e'(v' + \frac{1}{2}) - x'\omega_e'(v' + \frac{1}{2})^2] - [\omega_e''(v'' + \frac{1}{2}) - x''\omega_e''(v'' + \frac{1}{2})^2] \quad . \quad (\text{xxxiv.})$$

From a study of each band the appropriate value of  $\nu_0$  may be determined; if this is done for a series of bands resulting from one electronic transition, then from equation (xxxiv.) it should be possible to calculate the values of  $\omega_e'$  and  $\omega_e''$ . If the molecule is in its lowest electronic, *i.e.*, normal, condition in the lower state of the electronic transition, then  $\omega_e''$  will be equal to the equilibrium vibration frequency of the normal molecule. The value obtained in this way should naturally be identical with that calculated from infra-red spectra; for example, the equilibrium frequency of nitric oxide determined from various ultra-violet bands has been found to be about 1892, whereas the value from the vibration-rotation bands at  $2.65$  and  $5.3\mu$  is  $1895 \text{ cm.}^{-1}$ . As in the case of moments of inertia, already discussed, information concerning nuclear oscillations for homopolar molecules cannot be obtained from studies in the infra-red, and so the



ultra-violet spectrum provides in such cases one of the few available methods. It will be seen later that use may also be made of the Raman effect (p. 245).

### POTENTIAL ENERGY CURVES

As potential energy curves have proved very useful in the understanding of band spectra, and also in connection with photochemical and other problems, a short digression will be made here to explain their significance. The mutual force between the nuclei in a diatomic molecule, which may be taken as related to the potential energy, is the algebraic sum of an attractive and a repulsive force. When the constituent atoms are at an infinite distance apart the mutual forces, and the potential energy, are zero, but as they are brought closer together the attractive force at first predominates, so that the potential energy of the system decreases at first slowly and then more rapidly. As the nuclei approach further, however, the repulsive force increases more rapidly than the attractive force, and the system passes through a state of minimum potential energy which then increases very rapidly for smaller nuclear separations. The curve representing the variation of potential energy ( $U_r$ ) with the distance apart ( $r$ ) of the nuclei of a diatomic molecule may, therefore, be generally represented by a curve such as is shown in Fig. 15. When the potential energy is a minimum, at the point  $M$ , the molecule is in its most stable state, and the corresponding value of the nuclear separation ( $r_e$ ) may be taken as the equilibrium radius of the molecule; the negative of the potential energy is a measure of the energy which must be supplied in order to split up the molecule into its constituent atoms and so it is equal to the heat of dissociation ( $D$ ) of the compound. Attempts have been made to obtain a simple mathematical expression for the type of potential energy curve in Fig. 15, and one of the most useful of these is due to Morse (1929); it is

$$U_r = De^{-2a(r-r_e)} - 2De^{-a(r-r_e)} \quad . \quad . \quad . \quad (xxxv.)$$

where  $U_r$ ,  $D$ ,\*  $r$  and  $r_e$  are as already defined, and  $a$  is a constant

\* In this equation  $D$  includes the zero-point energy (*vide infra*); this is excluded in Fig. 15



for the given state of the molecule, being equal to  $\sqrt{8\pi^2cx\omega_e M/h}$ ,  $c$  is the velocity of light,  $M$  the reduced mass of the molecule (p. 194) and the other terms have the same significance as in equation (xviii.).

Since the atoms in a normal molecule vibrate the potential

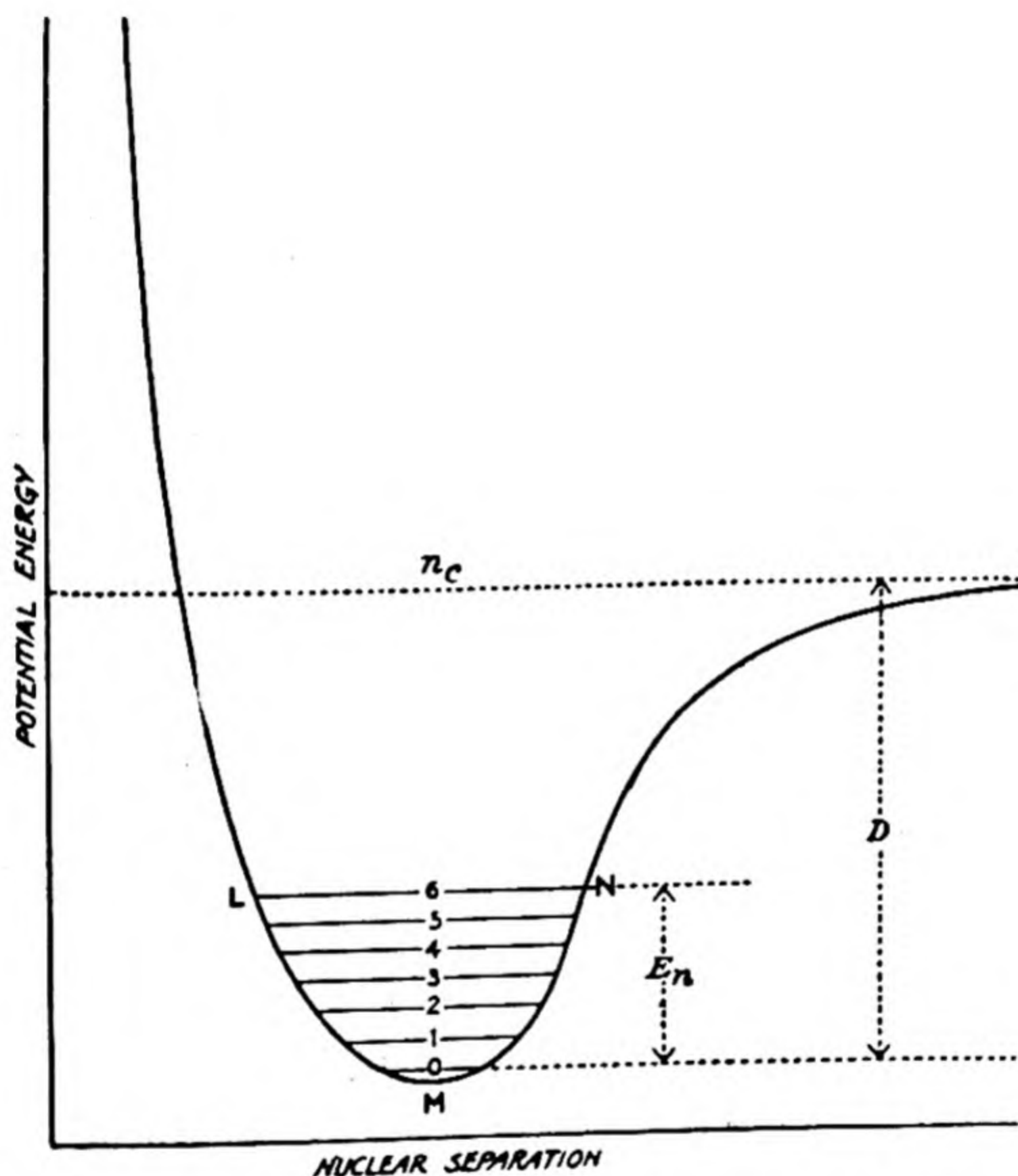


FIG. 15.—Type of curve representing the variation of potential energy ( $U_r$ ) of a diatomic molecule with distance apart ( $r$ ) of the nuclei.

energy will oscillate about the minimum position  $M$ , and the vibrational levels may be represented by the horizontal lines marked with the appropriate quantum numbers, 0, 1, 2, 3 (Fig. 15); the distance above  $n = 0$  gives the corresponding value of the vibrational energy  $E_n$  in excess of the "zero-point energy."\* Consider the line  $LN$ , representing the level for which the vibra-

\* The zero-point energy is the energy of the molecule when its vibrational and rotational quantum numbers are both zero; from equation (xviii.) it is evident that this is equal to  $\frac{1}{2}h\omega_e - \frac{1}{4}xh\omega_e$ . The importance of the zero-point energy is considered in "Recent Advances in General Chemistry," Chapters II. and IV.



tional quantum number is 6: as the molecule vibrates the potential energy changes, as the nuclei recede and approach, from  $L$  through  $M$  to  $N$  and back again for every vibration. If the motion were harmonic the curve  $LMN$  would be symmetrical about  $M$  and the whole potential energy curve would

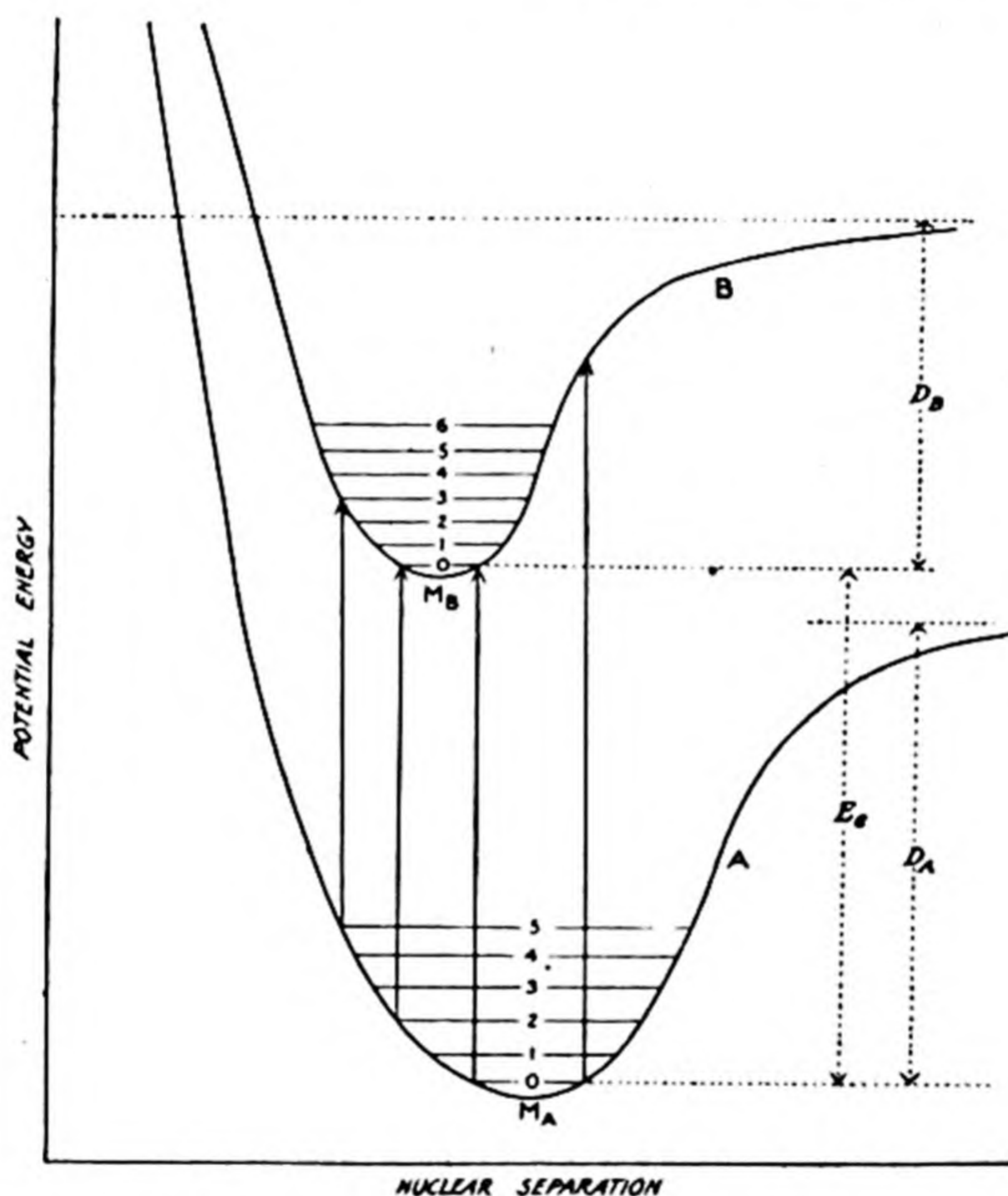


FIG. 16.—Potential energy curves for normal ( $A$ ) and excited ( $B$ ) states of a molecule, showing a number of Franck-Condon transitions.

be a parabola; this is approximately so for small values of the vibrational quantum number, but as it increases Fig. 15 shows that the symmetry disappears because of the anharmonic nature of the vibrations. It may be seen further that if the vibrational quantum number were large enough the nuclei would recede to infinity during the course of an oscillation; in other words, it should be possible to cause a molecule to dissociate by supplying



it with sufficient vibrational energy. Actually this type of dissociation rarely occurs in the normal state of the molecule, but it will be shown later that it is quite common in electronically excited states. The highest vibrational level which is theoretically possible for the molecule is marked  $n_c$  in Fig. 15.

Every electronic state of a molecule has its own specific potential energy curve which may have no relation whatever to that in another state; the greater the electronic energy the greater the potential energy of the system. Thus, the curves for a normal ( $A$ ) and an excited ( $B$ ) state of a molecule may be represented as in Fig. 16; an electronic excitation corresponds to a transfer from curve  $A$  to curve  $B$ . The conditions governing the transfer are given by the Franck-Condon principle which was proposed to account for the intensities of vibrational bands in electronic spectra; it states that a transition is most likely to occur when the nuclei are in their extreme positions, viz.,  $L$  and  $N$ , for example, in Fig. 15, and when it does occur the nuclear separation *at the instant* remains unchanged. The transition is consequently represented by a vertical line in the potential energy diagram, and a few possible cases are depicted in Fig. 16; an upward jump implies an absorption of energy and a downward move corresponds to emission. The Franck-Condon principle thus indicates the changes in vibrational quantum number resulting from an electronic transition. It will be noted that the equilibrium separations of the atomic nuclei, represented by the minima of the curves, are different in the two electronic states, and so also are the heats of dissociation; since the initial molecules and generally the resulting atoms are in different energy levels this is only to be expected. The vertical distance apart of the zero vibrational levels of the two curves  $A$  and  $B$  (Fig. 16) is a measure of the electronic energy difference ( $E_e$ ) between the two states.

The potential energy curves for different molecules or states may differ very considerably; for some substances the minimum of the curve for the excited state  $B$  will be to the left of that for the lower state  $A$ , for others it may be to the right, and in some instances the curves actually cross one another. Certain molecules appear to have excited states in which the potential energy curve



has no minimum (cf. Fig. 1, for hydrogen molecule with anti-symmetrical wave functions); in these cases the molecule can have no stability and such substances dissociate immediately they pass into that particular electronic state.

### HEATS OF DISSOCIATION

**Continuous Spectra.** It has been observed in a number of electronic spectra, *e.g.*, those of halogens, that the frequency separation for successive vibrational bands becomes smaller and smaller, on account of the anharmonic nature of the oscillator, and when the bands are so close together as to be indistinguishable there follows a region of continuous absorption or emission. The most careful examination has failed to show any fine structure in this type of continuous spectrum, and it can only be assumed that the molecule when absorbing, or emitting, the corresponding energy does not exist in a quantised state with definite energy levels. The explanation suggested for this behaviour by Franck (1925) is that with increasing vibrational quantum number the vibrational energy, and frequency of oscillation, of the nuclei constituting the molecule increases until a limiting value is reached; when this value is attained the vibrational bands converge. The absorption of a quantity of vibrational energy greater than this limiting amount is supposed to cause the molecule to dissociate into its constituent atoms so that the vibrations characteristic of the original molecule no longer occur; the region of quantised vibrational levels passes over into one in which there are no definite levels, but continuous absorption or emission of radiation. In other words, the vigour, or frequency, of oscillation of the parts of the molecule in the region of continuous absorption is so great that the vibrating portions break away from one another.

**Energy of Dissociation.** It seems reasonable to assume that at the spectral frequency corresponding to the convergence point of the vibrational bands the energy absorbed as radiation represents the minimum amount required to bring about dissociation of the molecule. The products of this dissociation are not always normal



atoms in their ground state, but, as will be seen shortly, they are often excited to an electronic level higher than the normal one. If due allowance is made for this excitation of one or both products it is often possible to calculate very accurate values for the heat of dissociation from spectroscopic data. The electronic spectrum of iodine vapour in the visible region shows a series of bands in the higher wavelength range followed by a region of continuous absorption commencing at a wavelength of about 5000 Å. By a short extrapolation, from 5030 Å, of the origins of the vibrational bands it is found that the convergence point is at 4995 Å; this value is related to the limiting vibrational energy of an iodine molecule. The energy acquired by the iodine at this point, that is the energy of dissociation, per single molecule is equal to the quantum corresponding to the wavelength of  $4995 \times 10^{-8}$  cm. According to the quantum theory

$$Q = h\nu = hc/\lambda \quad . \quad . \quad . \quad . \quad (\text{xxxvi.})$$

where  $c$  is the velocity of light, and  $\lambda$  the wavelength ; since  $h$  is  $6.547 \times 10^{-27}$  erg secs.,

$$Q = 6.547 \times 10^{-27} \times 3 \times 10^{10} / 4995 \times 10^{-8} \text{ ergs} . \text{ (xxxvii.)}$$

In order to convert this quantum into calories per gm. mol. it is necessary to multiply by the Avogadro number ( $6.062 \times 10^{23}$ ) and to divide by the mechanical equivalent of heat ( $4.185 \times 10^7$  ergs per calorie); the energy required to bring about the dissociation of a gm. mol. of iodine is thus found to be 56,950 calories. The value based on thermochemical measurements is about 35,000 calories per gm. mol., and so it is clear that in the dissociation of the iodine molecule by means of radiation the product cannot be two normal atoms of iodine.

The arc spectrum of atomic iodine consists of a number of doublets, the frequency separation of each being  $7600 \text{ cm.}^{-1}$  (wave-numbers); one line of the doublet is due to a normal atom, whereas the other line is caused by an excited atom. The frequency difference is proportional to the energy of excitation of the iodine atom; by the method already used it may be calculated that the energy difference between a normal and an excited atom is



21,650 cal. per gm. atom. If only one of the two iodine atoms is normal, and the other excited, in the dissociation of iodine molecules by means of radiation (*i.e.*, photochemical dissociation), the heat of dissociation into two normal atoms would be  $56,950 - 21,650 = 35,300$  calories per gm. mol. This value is very close to the quantity determined thermochemically (34,500 cal.), and in view of the great accuracy of which spectrum measurements are capable many authors consider the result so determined to be the more reliable. Similar methods have been used to calculate the heats of dissociation of chlorine and bromine molecules; the appropriate values are given in Table XLV.  $D'$  refers to the heat of dissociation into a normal and an excited atom, and  $D$  is the value for two normal atoms.

TABLE XLV

*Heats of Dissociation of Halogens (Calories per Gm. Mol.)*

Molecule.	Convergence Point.	$D'$ .	Excitation Energy.	$D$ Spectroscopic.	$D$ Thermochemical.
Chlorine .	4785 Å	59,400	2,500	56,900	57,000
Bromine .	5107	55,600	10,400	45,200	46,200
Iodine .	4995	56,950	21,650	35,300	34,500

**Dissociation and Continuous Spectra.** Apart from the excellent agreement between thermochemical and spectroscopic values for the heats of dissociation, further evidence has been obtained in favour of the view that dissociation occurs in the region of the continuous absorption spectrum. Iodine atoms have a very strong absorption line at 1830.4 Å, and normally molecular iodine vapour does not show decided absorption at this point. When illuminated by radiations from a carbon arc, however, which includes light of wavelength less than 4995 Å—the convergence point—Turner (1928) found that the 1830.4 Å line was more strongly absorbed. This result suggests that the molecules of iodine are dissociated into atoms as a consequence of exposure to the carbon arc.



Senftleben and Germer (1929) have detected the dissociation of halogen molecules into atoms under the influence of radiation by observing the change in resistance of a heated platinum wire placed in the gas exposed to the appropriate radiations. Dissociation into atoms causes the thermal conductance of the gas to increase; the temperature of the heated wire falls, and so also does its resistance, if dissociation occurs. In this way the higher wavelength limit for the radiation necessary to produce dissociation was found for the halogens, as follows:

Chlorine	$> 4722$ but $< 4800 \text{ \AA}$	Convergence point: $4785 \text{ \AA}$
Bromine	$< 5086 \text{ \AA}$	$5107$
Iodine	$< 5000 \text{ \AA}$	$4995$

The limiting wavelength for dissociation is in each case almost identical with the convergence point of the vibrational bands, and confirms the theory that the region of continuous absorption corresponds to dissociation of the molecules.

The direct spectroscopic method has also been used to determine the heat of dissociation of the hydrogen molecule; the electronic bands of this substance converge in the ultra-violet, and Dieke and Hopfield (1926) showed that at wavelengths smaller than  $849.4 \text{ \AA}$  absorption was continuous, indicating that dissociation occurs. The energy corresponding to this wavelength is  $334,000$  cal. per gm. mol., and there is good reason to believe that the products of dissociation are a normal and an excited atom. The energy of excitation of a hydrogen atom is known both from the critical potential (approx. 10 volts), and from the wavelength of the first line in the Lyman series of hydrogen ( $\lambda = 1216 \text{ \AA}$ ); the latter is due to a transition from the first excited level to the normal atom. Converting these values into cal. per gm. atom it is found that the energy of excitation is  $234,000$ ; the heat of dissociation of hydrogen into two normal atoms is, therefore,  $334,000 - 234,000 = 100,000$  cal. per gm. mol. The value determined by thermochemical methods is  $105,000 \pm 3,500$  cal. (Bichowsky and Copeland, 1928; see also Lozier, 1933).

The disappearance of the vibrational fine structure as a result of certain electronic transitions may also be studied from the



aspect of potential energy curves. Consider a molecule for which the lower and upper electronic energy levels are represented by the curves *A* and *B* in Fig. 17; if the state *A* absorbs energy it

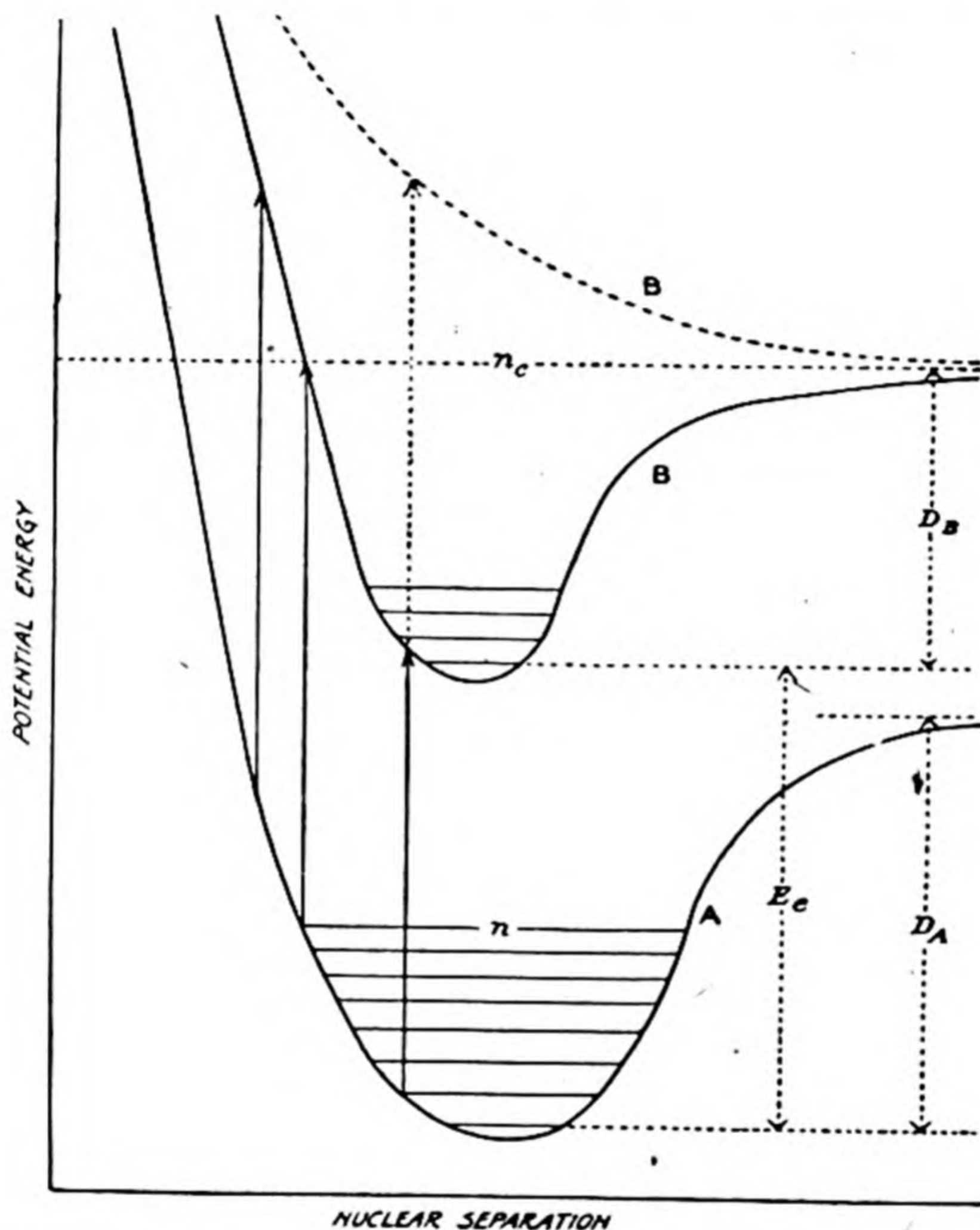


FIG. 17.—Potential energy curves for the normal (*A*) and two excited states (*B* and *B'*) of a molecule; transitions from *A* to *B* starting from vibrational levels above *n* lead to dissociation. All transitions from *A* to *B'* result in dissociation.

passes into *B* and by the Franck-Condon principle transitions are represented by vertical lines (p. 219). As long as the vibrational level in the state *A* is below that indicated by *n* the molecule in state *B*, after the transition, will still have definite vibrational



levels and the electronic spectrum will have vibrational bands. If the initial vibrational quantum number exceeds  $n$ , however, after the electronic transition the resulting molecule in the state  $B$  has a vibrational quantum number greater than  $n_c$ , which is the largest possible without dissociation occurring (p. 219); the molecule therefore dissociates. It may be supposed that immediately after the electronic transition the nuclei, which are at first close together, immediately start to recede, and their vibrational energy is so high that they recede to infinity. The vibrational band  $n \rightarrow n_c$  is, therefore, the last in the system  $A \rightarrow B$  to be observed; beyond this band the vibrational energy of the molecule is no longer quantised and there is continuous absorption, or emission if the change is  $B \rightarrow A$ . In order to bring about the dissociation of a molecule initially in the lowest vibrational level ( $v_A = 0$ ) of its normal, or ground, state  $A$ , it is consequently necessary to supply energy equivalent to  $\bar{E}_e + D_B$ ; the products of dissociation are those resulting from the decomposition of the molecule in the state  $B$ , and these, as already seen, are frequently excited.

As already mentioned, potential energy curves are of various types and by a consideration of them it is possible to account for various types of spectra. From the curves in Fig. 16 it can be seen that the particular transition to which they correspond will always give a band spectrum with vibrational quantisation, since there is no possibility of dissociation occurring in the  $A \rightarrow B$  transition except for such high levels in  $A$  that it is itself initially dissociated. Cases are known for which the potential energy curve in the excited state is represented by  $B'$  in Fig. 17, there being no minimum; *every* transition from  $A$  to  $B'$  results in dissociation, and so the spectrum is always continuous with no fine structure at all.

It will be noted that in this discussion of potential energy curves no reference has been made to the rotational energy of the molecules; as a rule this is small and may be ignored for the present purposes. There are a few instances, however, in which the rotation becomes so vigorous that it can bring about dissociation of the molecule; every rotational level then has a separate potential



energy curve within which there are definite vibrational energy levels as usual. As the rotational energy increases the minima in the curves become flatter until for a certain value of the rotational quantum number the curves become similar to *B'* Fig. 17; dissociation can then occur as the result of a rotational transition (Oldenberg, 1929; Villars and Condon, 1930). In the spectra of molecules exhibiting this type of behaviour, *e.g.*, HgH, the rotational structure after being sharp becomes diffuse and then ceases.

**The Method of Birge and Sponer.** For many molecules the vibrational bands cannot, for various reasons, be followed right up to the convergence point; in such cases Birge and Sponer (1926) suggested a method of extrapolation by means of which the heat of dissociation could often be calculated with reasonable accuracy. If a molecule were a truly harmonic oscillator the separation of successive vibrational bands would be constant and no convergence would be possible; for an anharmonic oscillator, however, the frequency and energy separations of the origins steadily diminish, and eventually become zero at the convergence point. By differentiating equation (xviii.) with respect to the vibrational quantum number  $v$ , it follows that

$$\frac{dE}{dv} = h\omega_e - 2(v + \frac{1}{2})xh\omega_e \quad . \quad . \quad . \quad (xxxviii.)$$

At the convergence point, which is designated by the quantum number  $n_c$  (see Figs. 15 and 17), the value of  $dE/dv$  becomes zero, since the vibrational energy has reached a limiting value; substituting  $n_c$  for  $v$  in equation (xxxviii.) and equating to zero, it is seen that

$$n_c = \frac{1}{2x} - \frac{1}{2} \quad . \quad . \quad . \quad . \quad . \quad (xxxix.)$$

If this is substituted in equation (xviii.) the vibrational energy at the convergence limit is given by

$$E_c = h\omega_e/4x \quad . \quad . \quad . \quad . \quad . \quad . \quad (xl.)$$

The energy required to bring about dissociation of the molecule is the difference between  $E_c$  and the amount of energy initially



possessed by the molecule: this may be taken as the zero-point energy, that is the vibrational energy for  $v = 0$ , which is  $\frac{1}{2}h\omega_e - \frac{1}{4}xh\omega_e$  (see footnote, p. 217); hence

$$D = h\omega_e/4x - (\frac{1}{2}h\omega_e - \frac{1}{4}xh\omega_e) \quad \text{. . . . . (xli.)}$$

The quantity  $D$  gives the energy of dissociation, virtually for the absolute zero of temperature. For many molecules, provided they do not contain hydrogen, the zero-point energy is relatively small, and the energy of dissociation may be represented by

$$D' = h\omega_e/4x \quad \text{. . . . . (xlii.)}$$

This is actually the dissociation energy with respect to the absolute zero of energy.

If the dissociation occurs in an excited state, represented, for example, by  $B$  in Figs. 16 and 17, then it is necessary to add to  $D$  as given by equation (xli.) the electronic energy  $E_e$ , which is equal to  $h\nu_e$  (see p. 212). The energy  $D^*$  required to dissociate the molecule from its ground state  $A$  to the products of the higher electronic state  $B$ , is then given by

$$D^* = D + h\nu_e \quad \text{. . . . . (xliii.)}$$

By means of these equations it is possible, often with fair accuracy, to calculate the heat of dissociation of a molecule, as the following examples will show.

**Heat of Dissociation of Hydrogen.** From a study of the electronic spectra of hydrogen it has been found that the lower vibrational levels in the ground state may be expressed by the equation

$$\nu = 4415.64(v + \frac{1}{2}) - 131.203(v + \frac{1}{2})^2$$

and so  $\omega_e$  is 4415.64 and  $x\omega_e$  is 131.203 cm.<sup>-1</sup> Substituting in equation (xlii.), it follows that

$$\begin{aligned} D' &= 6.547 \times 10^{-27} \times 3 \times 10^{10} \times (4415.64)^2/131.203 \times 4 \text{ ergs} \\ &\quad \text{per molecule} \\ &\equiv 105,600 \text{ cal. per gm. mol.} \end{aligned}$$

The zero-point energy is calculated from  $\omega_e$  and  $x\omega_e$  as 6,190 cal. and so the heat of dissociation of hydrogen is found to be 99,400 cal. per gm. mol. This may be compared with the value of 102,680 cal. obtained by Beutler (1984) by accurate graphical



extrapolation over a short range, which is in excellent agreement with the best value obtained by direct experimental observation (Lozier, 1933).

**Heat of Dissociation of Oxygen.** Analysis of the Schumann-Runge bands of molecular oxygen shows that the vibrational levels in the upper electronic (*B*) state may be represented approximately by

$$\nu = 49,052 + 710.14(v + \frac{1}{2}) - 11.705(v + \frac{1}{2})^2,$$

and by means of equations (xli.) and (xliii.) the value of  $D^*$  may be calculated, taking  $\nu_e$  as 49,052  $\text{cm.}^{-1}$ ; the result is found to be 169,100 cal. per gm. mol. If the particular state under discussion were dissociated it would probably yield a normal and an excited atom of oxygen; the energy of excitation of the latter is 1.96 volts, that is about 45,200 cal. It follows, therefore, that the heat of dissociation of molecular oxygen into two normal atoms is 123,900 cal. per gm. mol. By means of a short graphical extrapolation Knauss and Ballard (1935) obtained a value of 116,500 cal. The only direct experimental results available (Rodebush, 1930; Copeland, 1930) indicate that the heat of dissociation is about 130,000 cal., but it is highly probable that the spectroscopic value is the more accurate.

**Sources of Error in the Method of Birge and Sponer.** The main source of error in the calculation of the heats of dissociation by means of equations (xli.) or (xliii.) is based on the fact that the equation (xviii.) for the vibrational energy of an oscillator is not exact; strictly speaking, additional terms involving  $(v + \frac{1}{2})^3$ ,  $(v + \frac{1}{2})^4$ , etc., should be included, each with an appropriate anharmonic constant,  $y$ ,  $z$ , etc. If the latter are evaluated so that the resulting equation fits the observed vibrational band frequencies up to the highest observed values of  $v$ , then by following the treatment developed above for the simple equation more accurate values of the heat of dissociation would be obtained. As a general rule, however, it is simpler to carry out a graphical extrapolation, provided it has not to be carried too far. Birge (1929) has indicated the possibility that there may be a change in the direction of the curve representing the variation of the



frequency with the vibrational quantum number at a point beyond the last measured band, so that the extrapolation to the limiting convergence-point frequency may be in error. One of the cases, viz., the *B* level of oxygen, in connection with which this divergence was thought to occur, has now been shown to be quite normal (Knauss and Ballard), nevertheless it may exist in other instances. It is obvious, in general, that the most accurate results are obtainable in the simplest manner by graphical extrapolation to the point at which the curve of  $E$  or  $\nu$  against  $v$  has a slope of zero, provided the last measured band is not far from the theoretical convergence limit.

**Heats of Dissociation from Vibrational Spectra.** Strictly speaking the heat of dissociation of a molecule might be determined from measurements on the ordinary vibration spectrum of a molecule. It has been pointed out, however, that in reacting with infra-red radiation the vibrational quantum number rarely changes by more than two or three, and so an accurate extrapolation to the hypothetical convergence point would hardly be possible. Certain liquids, however, do give as many as eight or nine purely vibrational bands, and it will be shown in a subsequent section that in such cases heats of dissociation of linkages may be calculated from the measured frequencies.

### PRE-DISSOCIATION SPECTRA

**Diffuse Spectra.** In 1924 Henri observed that in the electronic spectrum of sulphur vapour not all the vibrational bands showed the expected rotational fine structure; from a given vibrational state, corresponding to a wavelength of 2792 Å, onwards, the bands appeared to be diffuse. Such diffuse bands were called by Henri "pre-dissociation" spectra, and have since been found to be produced by a large number of substances in addition to sulphur vapour, *e.g.*, sulphur dioxide, ammonia, nitrogen dioxide (Fig. 18), methyl halides and acetaldehyde. In some cases the pre-dissociation spectra are followed by a region of continuous absorption, but this is not always the case, as in certain other instances the diffuse bands are found on both long wave and short wave sides



of bands showing definite rotational lines. It appears to be generally accepted that in the production of the diffuse spectra a molecule is raised from one electronic energy level to another, and at the same time there are a number of definite vibrational transitions; the vibrational bands thus appear clearly in the electronic band system. If the energy acquired by a molecule in this transition is greater than that required to produce dissociation, then under certain circumstances the excitation energy may redistribute itself, with the result that the molecule dissociates. When the time elapsing between the acquisition of the necessary energy and its re-distribution is small compared with a period of rotation of the molecule, the latter will dissociate before a complete



FIG. 18.—Portion of the electronic band spectrum of nitrogen dioxide. The rotational fine structure is visible in the vibrational bands at 2491 and 2459 Å, but the bands at 2447 and 2425 Å are diffuse due to "pre-dissociation." (After Henri.)

rotation can occur; the rotation will thus not be quantised and the vibrational levels will not show fine structure.

The phenomenon of pre-dissociation may be examined in the light of potential energy curves; it is necessary to suppose that in addition to the excited level *B* there is another excited level *C*, the energy curve for which crosses that of *B* (Fig. 19). Normally direct transitions from *A* to *C* do not occur, although radiationless transitions, that is, involving no energy change, from *B* to *C* are possible, provided the potential energy of the former is in the vicinity of that represented by the point *P* (Fig. 19) where the curves for *B* and *C* cross. As a result of the transition  $A \rightarrow B$ , represented by the line I, the molecule in state *B* will vibrate normally and a vibration band with fine structure will result; for transition II., however, when the nuclei recede in state *B* the energy passes through the point *P* and a transition to state *C*



occurs. The energy of the system, although not great enough to dissociate state *B*, is now greater than that required to bring about dissociation of *C*, and so this occurs. The vibration in state *B* is still quantised, but for transitions like II., and beyond, the molecule dissociates, *via* state *C*, in less time than a period of rotation, and so the rotational fine structure ceases. Other types of pre-

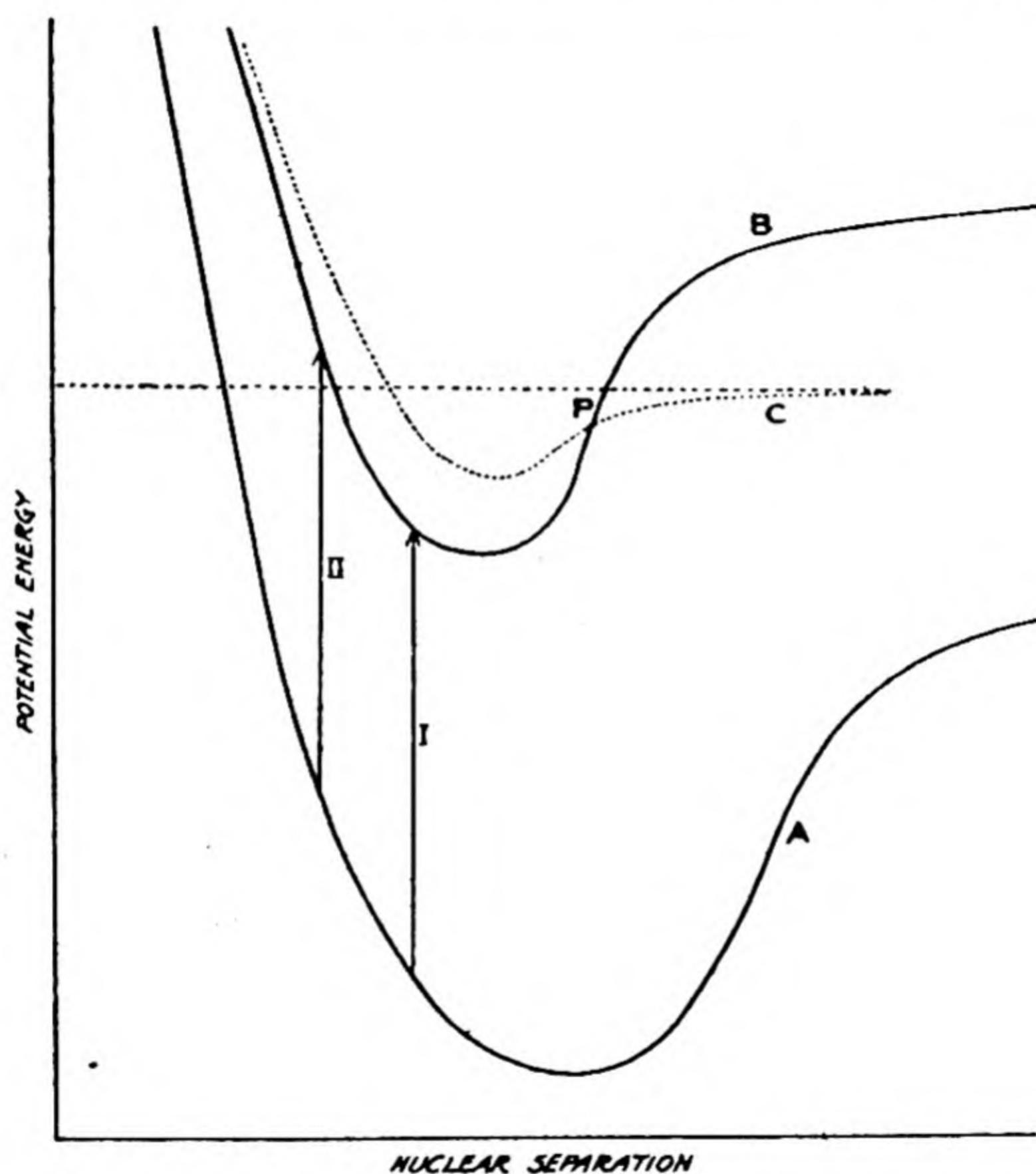


FIG. 19.—Potential energy curves of the normal (*A*) and two excited states (*B* and *C*) of a molecule, illustrating “pre-dissociation.”

dissociation are known, and these can be readily accounted for by appropriate potential energy curves; when the curves *B* and *C* cross at two points there are generally two pre-dissociation limits.

**Heat of Dissociation.** In the pre-dissociation region the excitation energy of a molecule must be at least equal to the heat of dissociation yielding the products of state *C*, and it is possible to calculate a maximum value for the normal heat of dissociation



from a knowledge of the wavelength at which the diffuse spectrum commences. For the sulphur vapour spectrum, which is due to  $S_2$  molecules, the diffuse band commences at 2794 Å; the corresponding energy of excitation is 102,000 cal. per gm. mol., and so the heat of dissociation of the  $S_2$  molecule may be taken as somewhat less than this value.

Henri has observed two pre-dissociation limits in the spectrum of nitrogen dioxide; these are at 3800 Å and 2459 Å, and are attributed to the formation of nitric oxide and a normal oxygen atom, and an excited oxygen atom, respectively. The corresponding heats of dissociation may, therefore, be calculated as

$$(a) \text{ NO}_2 = \text{NO} + \text{O (normal)} - 77,000 \text{ cal.}$$

and  $(b) \text{ NO}_2 = \text{NO} + \text{O (excited)} - 116,000 \text{ cal.}$

Since the heat of the reaction

$$(c) \text{ NO}_2 = \text{NO} + \frac{1}{2}\text{O}_2 - 13,000 \text{ cal.}$$

is known from thermal measurements, it follows from (a) and (b) that

$$\text{O}_2 = 2\text{O (normal)} - 128,000 \text{ cal.}$$

Further, since the energy difference of a normal and excited oxygen atom is known to be about 45,000 cal. (p. 228), it may be shown that the second pre-dissociation limit yields a heat of dissociation of 123,000 cal. for the oxygen molecule into normal atoms. These results are in excellent agreement with those already discussed.

(For further aspects of pre-dissociation spectra, see Chapter VI.)

## ISOTOPES

**Isotopes of Oxygen.** One of the most notable achievements of the study of band spectra has been the discovery by its means of two new isotopes of oxygen, one of carbon, one of nitrogen, and possibly one of beryllium. It had been noted that in the electronic spectrum of molecular oxygen, in which the two combining states were the first excited level and the normal electronic level, there appeared a faint band, the  $A'$  band, being an exact duplication of



a well-defined band, the  $A$  band. The faint lines, actually doublets, of the  $A'$  band alternated with the strong lines of the  $A$  band, but the spacing was not quite regular, as the rotational separations for the two bands were slightly different. Giauque and Johnston (1929) suggested that the  $A'$  band resulted from the presence in oxygen gas of an isotope of atomic weight 18. By assuming that the strong lines were due to a molecule containing two atoms of atomic weight 16, and the weak lines to a molecule consisting of one atom of weight 16 and one of 18, the separations of consecutive lines could be calculated; the values obtained in this manner were found to be in excellent agreement with those observed in the spectrum.

**Isotopic Separation.** The method of calculation is roughly as follows. Suppose  $\omega_1'$  and  $\omega_2'$  represent the equilibrium vibration frequencies of the two isotopic molecules in the upper electronic state, and  $\omega_1''$  and  $\omega_2''$  the corresponding values in the lower state, then by the application of equation (xxix.), p. 208, it follows that

$$\frac{\omega_1' - \omega_2'}{\omega_1'} = 1 - \rho, \therefore \omega_1' - \omega_2' = \omega_1'(1 - \rho). \quad (\text{xliv}.a)$$

and also

$$\frac{\omega_1'' - \omega_2''}{\omega_1''} = 1 - \rho, \therefore \omega_1'' - \omega_2'' = \omega_1''(1 - \rho). \quad (\text{xliv}.b)$$

where  $\rho$  is equal to  $\sqrt{M_1/M_2}$ , that is the square root of the ratio of the reduced masses. If  $\nu_1$  represents the frequency of the origin of a particular vibrational band for one of the isotopic forms, then from equation (xxxiii.) it is possible to write

$$\nu_1 = \nu_e + \omega_1'(v' + \tfrac{1}{2}) - \omega_1''(v'' + \tfrac{1}{2}) \quad . \quad (\text{xxxiii}.a)$$

assuming the oscillations to be harmonic. Similarly if  $\nu_2$  is the frequency of the origin of the corresponding band for the other isotope, then

$$\nu_2 = \nu_e + \omega_2'(v' + \tfrac{1}{2}) - \omega_2''(v'' + \tfrac{1}{2}) \quad . \quad (\text{xxxiii}.b)$$

Hence the isotopic "shift" of the band origin,  $\nu_1 - \nu_2$ , is given by

$$\nu_1 - \nu_2 = (\omega_1' - \omega_2')(v' + \tfrac{1}{2}) - (\omega_1'' - \omega_2'')(v'' + \tfrac{1}{2}) \quad . \quad (\text{xliv}.)$$



and by the use of equations (xliv. *a* and *b*) it follows that

$$\nu_1 - \nu_2 = \omega_1'(1 - \rho)(v' + \tfrac{1}{2}) - \omega_1''(1 - \rho)(v'' + \tfrac{1}{2}) \quad . \quad . \quad (\text{xlvi.})$$

This formula gives the value of isotopic shift in the general case; this shift is greater the smaller the value of  $\rho$ , and hence the smaller the mass of the isotopic atom. With boron the isotopes having atomic weights of 10 and 11 respectively, and so the value  $\nu_1 - \nu_2$  is quite large. In Figs. 11 and 14 is seen a portion of the  $\beta$ -system of BO, and each vibrational band is observed to appear in duplicate; the upper and lower quantum numbers for each band are indicated: the dotted lines represent those for the lighter, and rarer, isotope.

In the particular example under discussion, namely oxygen, it has been found that the *A* band is the fundamental of the series corresponding to the electronic transition from the ground level to the first excited level, and that both initial and final vibrational quantum numbers ( $v'$  and  $v''$ ) are zero. Hence the equation for the isotopic shift of the frequency of the origin of the *A* band becomes

$$\nu_1 - \nu_2 = \tfrac{1}{2}(1 - \rho)(\omega_1' - \omega_1'') \quad . \quad . \quad (\text{xlvi.}a)$$

If  $\omega_1$  and  $\omega_1''$  are taken as referring to the isotope of mass 16, then the values are known from an analysis of the band group corresponding to the transition from normal to the first excited state, of which the *A* band is the first. The actual equilibrium vibration frequencies are 1415.017 and 1565.37  $\text{cm.}^{-1}$  respectively. Substituting the appropriate values for the atomic masses in the formulæ for the reduced masses  $M_1$  and  $M_2$  (equation (xi.), p. 194), where  $M_1$  refers to the  $^{16}\text{O}^{16}\text{O}$  molecule, and  $M_2$  to the  $^{16}\text{O}^{18}\text{O}$  molecule, it is found that  $\nu_1 - \nu_2$  is equal to  $-2.053 \text{ cm.}^{-1}$ . The origin of the *A'* band, if due to a molecule containing two isotopic atoms of mass 16 and 18 respectively, should thus be displaced by a frequency of  $2.053 \text{ cm.}^{-1}$  from the origin of the *A* band, the frequency of the latter being the greater. The actual frequency displacement observed was  $2.067 \text{ cm.}^{-1}$ , and the small discrepancy may be readily accounted for by making an allowance for the anharmonic oscillation of the nuclei in the molecules. The agreement found after making the necessary corrections (Birge, 1929)



is very striking, and confirms the view concerning the existence of the isotope of oxygen with an atomic weight of 18. The frequency separation of corresponding rotational lines would also be  $2.06 \text{ cm.}^{-1}$  were it not for the fact, already mentioned, that molecules containing different isotopes will have different rotational spacings. The isotopic rotational shift is given by  $mb(1 - M_1/M_2)$ , where  $m$  is the integer used in the equation for the frequencies of rotational lines (see p. 198); for the isotopic oxygen molecules this reduces to  $0.0556 mb \text{ cm.}^{-1}$ . This result is only approximate, since no allowance has been made for the difference in the moments of inertia in the initial and final states of the molecule; when the appropriate correction, determined from spectral data, is applied the agreement between calculated and observed frequency separations of corresponding lines in the  $A$  and  $A'$  bands is very good.

**Symmetrical and Unsymmetrical Oxygen Molecules.** A striking confirmation of the existence of the 18 isotope of oxygen was obtained in another manner depending on the examination of band spectra. It has been observed that in the strong electronic bands of oxygen alternate rotational lines are missing, and only those with odd rotational quantum numbers are present. According to modern quantum mechanics this is what is to be anticipated for a symmetrical molecule of which the constituent nuclei have no spin momentum (see p. 198). In the  $^{16}\text{O}^{18}\text{O}$  molecule, however, the symmetry is destroyed, and all the rotational levels should exist; the  $A'$  band should thus contain twice as many lines as the  $A$  band. A number of these additional faint lines had been observed in the early studies of the band spectrum of oxygen, but as they did not fit in with the lines of the  $A$  band they were ignored; later it was shown that these lines, together with others discovered subsequently, complied exactly with the requirements of the isotopic form of oxygen. A further examination of the spectrum revealed the presence of a series of lines still fainter than those of the  $A'$  band, and Giaque and Johnston (1929) showed that these were due to the presence of another isotopic molecule  $^{16}\text{O}^{17}\text{O}$ , involving a second isotope of atomic weight 17. From the intensities of the various lines it has been concluded that the relative proportions of the isotopes of oxygen of atomic weight



16, 18 and 17 are 3,150 to 5 to 1, respectively (Mecke and Childs, 1931). Later estimates give the proportions of  $^{16}\text{O}$  to  $^{18}\text{O}$  as  $520 \pm 20$  to 1 (Smythe, 1934 ; Manian, Urey and Bleakney, 1934).

**Isotopes of Carbon.** From an examination of the so-called Swan bands of burning hydrocarbons, which are apparently due to the  $\text{C}_2$  molecule, Birge and King (1929) found evidence for the existence of an isotope of carbon of mass 13. This view has been confirmed by the discovery of a series of faint lines, separated from the main strong lines by the requisite isotopic shift, in the band spectra of carbon monoxide and of cyanogen. There seems very little doubt, therefore, that carbon has two isotopes, at least, with masses of 12 and 13 respectively ; the proportion of the two isotopes is about 100 to 1 (Jenkins and Ornstein, 1932 ; Tate, Smith and Vaughan, 1933).

**Isotopes of Nitrogen.** The third element in which hitherto unsuspected isotopes have been discovered by spectroscopic methods is nitrogen. When making a careful study of the electronic absorption spectrum of nitric oxide, Naudé (1929–1930) observed a series of lines with frequency separations equal to those anticipated for the molecules  $^{14}\text{N}^{16}\text{O}$ ,  $^{14}\text{N}^{18}\text{O}$ ,  $^{14}\text{N}^{17}\text{O}$  and  $^{15}\text{N}^{16}\text{O}$ . These results not only confirmed the existence of the three isotopes of oxygen, but implied the presence of an isotope of nitrogen of atomic weight 15.00. From the relative intensities of various lines it was concluded that the ratio of the  $^{14}\text{N}$  to the  $^{15}\text{N}$  isotopes in ordinary nitrogen is about 850 to 1 (Murphy and Urey, 1932).

**Deuterium.** Although deuterium was discovered by its atomic spectrum, a great deal of valuable information has been obtained by the study of the band spectra of its compounds. This subject is considered in the chapter on deuterium in "Recent Advances in General Chemistry."

## BAND SPECTRA OF LIQUIDS

**Infra-red Spectra.** Substances which are liquid at ordinary temperatures generally contain many more than two atoms in the molecule, and so the number of vibrational and rotational changes and electronic transitions is very large. It is not to be wondered



at, therefore, that the spectra of liquids are difficult to interpret in detail, although some general indications have been obtained. Much work has already been done on the ultra-violet absorption spectra of organic compounds, but apart from the fact that related substances have similar absorption bands very little more can be said with any degree of certainty. It has been urged for some time, however, mainly by Coblentz (1905 *et seq.*), that the presence of certain absorption bands in the infra-red region of the spectrum is associated with definite chemical groups. In recent years this view, although not universally accepted, has obtained much support, and it is considered that the frequencies of the absorption maxima are related to the equilibrium vibration frequencies of the atoms involved in a definite linkage.

### THE C — H LINKAGE

For example, all aliphatic compounds containing the C — H grouping have an absorption maximum situated at a wavelength of about  $3.4\mu$ , with sometimes a harmonic at  $1.7\mu$ ; these bands do not appear for substances in which there is no hydrogen atom linked directly to carbon. The actual position of the absorption maximum changes somewhat with the nature of the compound in which it occurs; the variation is generally between the limits of wavelength of  $3.2$  to  $3.5\mu$ , and is not surprising since the residue of the molecule to which the C — H is attached is certain to influence the oscillations of the C and H atoms towards one another (*vide infra*, p. 250). In aromatic compounds the C — H band is found at  $3.25\mu$ , and it is perhaps significant that this is the position of the maximum absorption for aliphatic compounds containing the — C = CH grouping. The change from  $3.4$  to  $3.25\mu$  is not due to ring formation, as the former is the wavelength of the absorption maximum for piperidine, in which there is a six-membered ring but no double linkage; pyridine, on the other hand, has an absorption maximum at  $3.25\mu$ . Hence it may be inferred that the study of infra-red spectra favours the Kekulé formula for benzene.

Some confirmation of the view that the  $3.2$  to  $3.5\mu$  bands in



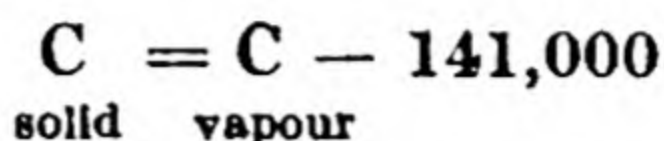
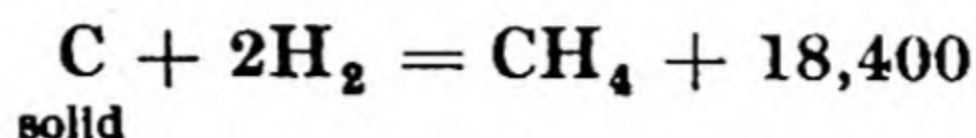
organic compounds are due to the atomic vibrations in the C — H grouping has been obtained from two directions. The emission spectra of burning hydrocarbons contain two electronic band systems which, there is good reason to believe, are due to transitions in a CH molecule only existing at the high temperatures of flames; examination of the vibrational bands of these systems indicates that the equilibrium vibration frequency ( $\omega_e$ ) of CH in its "normal," or ground, state is  $2800\text{ cm.}^{-1}$ . The frequency corresponding to the observed absorption spectra of organic compounds in the infra-red, and believed to be due to the C — H group, is the reciprocal of the wavelength  $3.2$  to  $3.5\mu$ , that is,  $2860$  to  $3125\text{ cm.}^{-1}$ . The agreement with the value from electronic band spectra supports the theory suggested concerning the origin of  $3.2$  to  $3.5\mu$  absorption maximum.

**Heat of Dissociation.** Another line of argument has been followed by Ellis (1929); this author identified eight absorption bands in the spectrum of benzene as forming an anharmonic vibrational series from  $0.476\mu$  to  $3.27\mu$  in wavelength. Like the  $3.27\mu$  fundamental these absorption maxima were attributed to oscillations of the atoms concerned in the C — H linkages present in the benzene molecule. It can be shown from equation (xviii.) that the frequency separation of successive vibrational bands is equal to  $\omega_e - 2vx\omega_e$ , and it has been found that the frequency separations of the eight bands of benzene, observed by Ellis, can be represented by  $3083 - 115v$ ; hence  $\omega_e$  is  $3083\text{ cm.}^{-1}$  and  $x\omega_e$  is  $57.5$ . If it may be assumed that the same expression applies for the separation up to the convergence point (p. 220), the energy of dissociation of the C — H linkage, evaluated by equation (xlii.), is found to be  $118,000$  cal. per gm. mol. Similar calculations made by Ellis for the heat of dissociation of C — H bonds in hexane, cyclohexane and chloroform gave values of  $97,000$ ,  $94,000$  and  $108,000$  cal. respectively. Allowance for the zero-point energy would reduce these figures by about  $3,500$  cal.

An approximate determination of the heat of formation, and hence of dissociation, of a C — H linkage may be made as follows. The heat of formation of methane from solid carbon and molecular hydrogen is known to be about  $18,400$  cal.; the heat of dissocia-



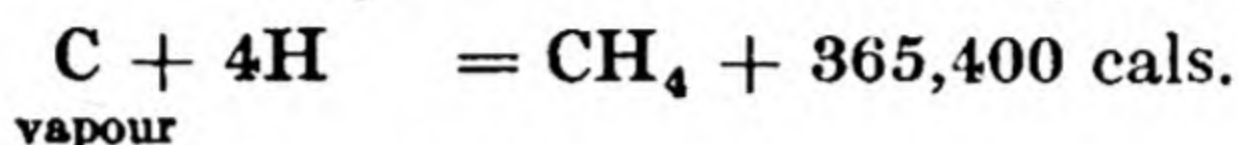
tion of hydrogen into atoms is 103,000 cal. per gm. mol., and the heat of sublimation of carbon is 141,000 cal. per gm. atom; that is



and



Hence



Since the formation of the methane molecule involves the establishment of four C — H linkages, the heat evolved per linkage is approximately 91,400 cal. per gm. mol.; the heat of dissociation should, of course, have the same value. This result is somewhat lower than the heat of dissociation of the same linkage determined from spectroscopic data, but in view of the doubtful accuracy of the straight line extrapolation in the Birge and Sponer method, and the uncertainty in some of the thermal values the agreement may be considered to favour the view that definite absorption spectra may be associated with the oscillations of the C — H group. In any case the dissociation energy will certainly vary with the nature of the other groups present in the organic molecule, and so exact agreement and constancy for all compounds is not to be expected. There is, in fact, reason to believe that the mean heat of dissociation of the C — H linkage in benzene is 101,000 cal. per gm. mol., rather than the smaller value calculated from the thermal data connected with the formation of methane.

### THE N — H LINKAGE

It is generally accepted that the oscillations of the N — H group are the cause of an absorption maximum at 2.9 to 3 $\mu$ ; this band not only occurs with ammonia but with all primary and secondary, although not tertiary, amines. Ellis has suggested that six absorption bands of ammonia are part of a vibrational series due to the N — H linkage, with a fundamental band at 2.9 $\mu$ ; proceeding in the same manner as for the C — H group in benzene it has been calculated that the heat of dissociation of N — H is 118,000 cal., whereas the thermochemical value is 92,000 cal.



per gm. mol. Other bands in the infra-red region of the spectrum have been identified with various groupings, *e.g.*, O — H, C — C, C — Cl, C — Br and C — I, but in view of the experimental difficulties the data are not yet definitely established; interesting information has been obtained, however, from a study of the Raman effect (*vide infra*, p. 243).

Objection has been made by Bell (1928) to the view that certain linkages produce definite absorption bands on the grounds that some isomeric substances, *e.g.*, dibutyl and di-isobutyl carbonates, containing the same number of C — H linkages, do not have the same *intensity* of absorption in the infra-red. It is very improbable, however, that in a complex molecule the effect of the C — H linkages will be exactly additive; interaction between different groups will affect the total intensity, and this will vary from compound to compound apart from the actual number of groups present. The objection cannot, therefore, be regarded as convincing.

### BAND SPECTRA OF SOLIDS

A number of observations has been made on the infra-red absorption spectra of solids, particularly crystals of simple salts like carbonates, sulphates and nitrates. The oscillations of the lattices constituting a crystal, against one another, should give rise to a definite spectrum, but as such vibration frequencies are likely to be small the corresponding radiations would be in the far infra-red. This type of spectrum has been studied mainly by Rubens (1897–1914), but the results have not yet been given any physico-chemical significance. In addition the more rapid vibrations of the atomic nuclei in the crystal lattice result in the absorption of radiation in the near infra-red, and it has been found that the spectra for different salts of the same acid, *e.g.*, carbonates, are almost identical; these are evidently due to the anion group ( $\text{CO}_3''$ ), and so support is provided for the view, advanced from a study of crystal structure by means of X-rays, that in a salt the lattices are made up of ions and not molecules. The frequencies of all the absorption bands of carbonates can be expressed in terms of four fundamental frequencies, three of which



actually appear in the spectrum. The corresponding oscillations are probably (a) two, represented by  $\omega_1$  and  $\omega_2$  in Table XLVI. below, in the plane of the  $\text{CO}_3$  group which, according to Bragg, consists of three oxygen atoms at the corners of an equilateral triangle with the carbon atom at the centre, and (b) one perpendicular to the plane of the group ( $\omega_3$ ). The vibrations which are inactive optically ( $\omega_0$ ) and produce no spectrum are most likely due to the oscillations of the three oxygen atoms towards the central carbon atom; these vibrations produce no change in the electric moment of the molecule and so do not react directly with radiation. Combination tones between this inactive frequency and the active ones seem to be possible, and it is from these that the value of the inactive frequency can be estimated. The existence of this inactive oscillation has been confirmed by means of the Raman spectrum. The infra-red absorption spectra of a number of carbonates have been studied by Schaefer and his co-workers (1926-7) and by Rideal (1927); some of the results obtained for the fundamental oscillation frequencies  $\omega_1$ ,  $\omega_2$ ,  $\omega_3$  and  $\omega_0$  are given in Table XLVI.

TABLE XLVI

*Fundamental Vibration Frequencies ( $\text{Cm.}^{-1}$ ) of Carbonates*

Fundamental.	$\text{MgCO}_3$ .	$\text{CaCO}_3$ .	$\text{SrCO}_3$ .	$\text{BaCO}_3$ .	$\text{PbCO}_3$ .
$\omega_1$ . . .	1495	1492, 1429	1475	1460, 1409	1420, 1374
$\omega_2$ . . .	725	706	697	690	667
$\omega_3$ . . .	889	879	866	861	833
$\omega_0$ (Inactive) .	1065	1099	—	1045	989

An interesting conclusion has been reached as the result of a closer examination of the spectra of these salts; it has been found that with calcite, and other uni-axial carbonates (Schaefer, 1927), two of the fundamental frequencies,  $\omega_1$  and  $\omega_2$ , which are apparently connected with the vibrations in the plane of the  $\text{CO}_3$  group, are really doublets. This doubling has been shown, from



a mathematical study of symmetry, to be impossible if the three oxygen atoms are at the corners of an equilateral triangle ; if this triangle is distorted, even very slightly, so as to produce an isosceles triangle, the two pairs of fundamental vibrations become theoretically possible. Pauling (1931) concludes, however, from wave mechanical considerations (see p. 70) that the  $\text{CO}_3$  ion has a pyramidal and not a planar structure: the oscillation of the carbon atom above and below the plane containing the symmetrically situated oxygen atoms would be the cause of the doublets.

As is to be expected the infra-red spectra of nitrates are very similar to those of carbonates, but the sulphates show a different behaviour ; the  $\text{SO}_4$  ion is probably arranged in the form of a regular tetrahedron with the oxygen atoms at the corners and the sulphur atom at the centre. Such an arrangement, which corresponds to that of the methane molecule, should give two active fundamentals and one inactive frequency ; the former are established, at least approximately, but very little appears to be known of the latter. Further investigation on sulphates is required before any definite conclusions can be reached concerning the symmetry of the ion. Potassium chromate, perchlorate and permanganate have infra-red spectra similar to that of potassium sulphate (Taylor, 1929), except that as the size of the central atom increases, and the oxygen atoms are further removed from the centre, the oscillation frequency, as might be expected, decreases. An increase of ionic charge, however, often causes a more rapid vibration to occur, on account of the increase in the magnitude of the restoring force. The results in Table XLVII. illustrate these points.

TABLE XLVII

*Fundamental Vibration Frequencies ( $\text{Cm.}^{-1}$ ) of  $\text{XO}_4$  Salts*

Fundamental.	$\text{K}_2\text{SO}_4$ .	$\text{K}_2\text{CrO}_4$ .	$\text{KClO}_4$ .	$\text{KMnO}_4$ .
$\nu_1$ . .	625	550	720 ?	400 ?
$\nu_2$ . .	1092	870	1080	888



Although very little systematic study of the spectra of solids has yet been made it is clear that such work, especially in conjunction with the Raman spectrum (p. 256), may lead to interesting results in connection with the problems of molecular architecture.

## THE RAMAN EFFECT

**The Scattering of Light.** In the course of a comprehensive investigation of the scattering of light by liquids Raman (1928) discovered that in the scattered light there were radiations of different frequencies from that of the incident light, and that the frequency differences were characteristic of the scattering liquid. The amount of scattered light is generally very small, but it can be studied by means of a spectrometer with photographic attachment, so that exposures of many hours' (8 to 100) duration can be made. This alteration, or displacement, of frequency—often called the Raman effect, or the Smekal-Raman effect since it had been predicted theoretically by Smekal (1923)—has been shown to be a very general phenomenon and to occur with all phases of matter under a great variety of conditions. Information concerning the origin of the Raman scattered lines may be obtained in the following manner. (If  $\nu_i$  represents the frequency of the incident radiation and  $\nu_s$  that of the scattered light, where  $\nu_s$  is generally less than  $\nu_i$ , then by the quantum theory the energy associated with the incident and scattered rays is  $h\nu_i$  and  $h\nu_s$ , respectively; the energy difference, which has presumably been transferred to the molecules of the substance under examination, is equal to  $h(\nu_i - \nu_s)$ . The frequency of the oscillations absorbing this radiation must then be  $\nu_i - \nu_s$  ( $= \Delta\nu$ ); this is called the Raman frequency.

The mechanism of the Raman effect, which is based on quantum mechanics and generally accepted at present, is that a molecule in a level  $A$  with energy represented by  $E_A$  absorbs the incident radiation and is thereby raised to a level  $C$ , in which its energy is  $E_C = E_A + h\nu_i$ . The molecule then emits the observed Raman radiation of frequency  $\nu_s$ , and in so doing falls to an intermediate level  $B$ , wherein its energy  $E_B$  is equal to  $E_C - h\nu_s$ . The net gain of energy by the molecule is thus



$$\begin{aligned} E_B - E_A &= h(\nu_i - \nu_s) \\ &= h\Delta\nu. \end{aligned}$$

For the production of the Raman scattering it is therefore necessary to have three energy levels for the molecule which are able to "combine" in conformity with the ordinary selection rules. The levels *A* and *B* are the initial and final states, whereas *C* is called the "intermediate" or "common" level. In some cases the level *B* is below that of *A*, so that  $\nu_s$  is greater than  $\nu_i$ , the molecule having given up its energy to the scattered radiation; under these conditions

$$\nu_i - \nu_s = \Delta\nu.$$

When  $\Delta\nu$  is positive the Raman spectrum is said to consist of "Stokes lines," and when it is negative the spectrum consists of "anti-Stokes lines"; the former occur much more frequently than the latter. Both types may be seen about the 4358 line in Fig. 20.

**Raman Frequency and Molecular Vibration.** Actual examination of Raman spectra has shown that the value of  $\Delta\nu$  is generally of the order of 500 to 5000  $\text{cm.}^{-1}$ , and so corresponds to the oscillation frequencies of atoms as determined from vibration spectra in the infra-red, and from the vibrational bands of electronic spectra. It may be concluded, therefore, that the energy change from the incident to the scattered light is equal to that absorbed in raising the vibrational energy of the molecule from one level to another. According to this view the lowest Raman frequency for a molecule should generally be almost equal to its equilibrium vibration frequency (see equation (xxii.), p. 202). Further, the wavelengths corresponding to the Raman frequencies ( $\Delta\nu$ ) should be the same as the wavelengths of the centres of the vibrational bands of the molecule in the near infra-red. In Table XLVIII. are given the values of  $\Delta\nu$ , the scattered frequency displacement, and the corresponding wavelengths, together with the positions of the known vibration bands for carbon dioxide and for hydrogen chloride. In the Raman spectrum of each of these substances there are three lines which correspond evidently with the fundamental vibration band and its first and second harmonics.



TABLE XLVIII.—*Raman Frequencies and Infra-Red Bands*

Carbon Dioxide.			Hydrogen Chloride.		
Raman.		Infra-red.	Raman.		Infra-red.
$\Delta\nu$	$\lambda$	$\lambda$	$\Delta\nu$	$\lambda$	$\lambda$
2155 cm. <sup>-1</sup>	4.64 $\mu$	4.52—4.67 $\mu$	2890 cm. <sup>-1</sup>	3.46 $\mu$	3.48 $\mu$
4294	2.33	2.35—2.48	3656	1.77	1.76
6387	1.567	1.57	8298	1.205	1.190

Although homopolar molecules cannot yield pure vibration spectra (p. 199), they do give the Raman effect in scattered light, and the frequency displacement is, as in other cases, equal to the equilibrium vibration frequency of the molecule. The truth of this statement is borne out by a comparison in Table XLIX. of the Raman frequency change for liquid oxygen, nitrogen and hydrogen (McLennan, 1929) with the equilibrium vibration frequencies for the same molecules determined from the electronic band spectra of the gases.

TABLE XLIX.—*Raman Frequencies and Equilibrium Oscillation Frequencies of Homopolar Molecules*

Frequencies (cm. <sup>-1</sup> ).				
	Exciting Radiation $\nu_i$	Scattered Radiation $\nu_s$	$\nu_i - \nu_s$ $= \Delta\nu$	Band Spectra $\omega_e$
Oxygen .	24,705	23,154	1554	1554
	22,938	21,387	1551	
Nitrogen .	24,705	22,371	2335	2331
	22,938	20,616	2322	
Hydrogen .	24,705	20,556	4149	4159

The agreement is on the whole very good and lends support to the ideas expressed here as to the origin of the Raman spectrum. These results incidentally bring out the fundamental nature of the Raman effect since it appears to be independent of the physical



state of the substance; for the three elements whose Raman displacements are given in Table XLIX. for the liquid state, the values for the gases are 1555, 2331 and 4162  $\text{cm.}^{-1}$  respectively.

**Raman Spectra and Molecular Models.** Andrews (1930) and his co-workers have devised an ingenious method for identifying Raman lines with particular vibrations in a molecule, by means of suitable models. In these models steel balls represent nuclei and springs valency bonds, the relative masses, strengths and dimensions being the same as in a single molecule. The appropriate model is suspended by elastic bands and attached to an arm which can be made to oscillate at various frequencies; at certain definite rates of vibration, but not at intermediate values, the model moves in resonance with the arm. These may be regarded as the equilibrium vibration frequencies of the particular linkages in the corresponding molecule, and when recalculated to true molecular dimensions the values so obtained show a remarkable parallelism with those derived from Raman spectra.

**Isotopes.** If a molecule contains two isotopic forms of the same atom the fundamental oscillation frequencies for the two types of molecule will be different. In these circumstances the Raman line corresponding to the particular vibration involving the isotopic atom will actually be a doublet, one line for each isotopic form; the theoretical frequency separation may be calculated by means of equation (xxix.), p. 208. It has been claimed that the expected fine structure has been observed in the Raman spectrum of carbon and tin tetrachlorides (Langseth, 1931).

**Raman Frequency and Molecular Rotation.** The Raman effect does not always result from a change in the vibrational energy

TABLE L.—*Raman Frequencies for Liquid Hydrogen*

Frequencies ( $\text{cm.}^{-1}$ ).			
Exciting ( $\nu_i$ ).	Scattered ( $\nu_s$ ).	Raman ( $\nu_i - \nu_s$ ).	Band Spectra Frequencies.
22,938	22,584	354	347
22,938	22,350	588	578



of the molecules of the substance dispersing the light. In addition to the data already given for hydrogen (Table XLIX.), the following values for the frequencies of exciting and scattered radiation, with the mercury line of wavelength  $4358.3 \text{ \AA}$ , *i.e.*, frequency  $22,938 \text{ cm.}^{-1}$ , were obtained by McLennan (Table L.).

The difference in frequency between the exciting and scattered radiations is too small to be explicable by any oscillations in a light molecule like that of hydrogen, but the observed values (column 3) agree with the frequency differences for certain *rotational* levels, as determined from electronic spectra. The actual values given in the last column correspond to rotational transitions from  $J = 0$  to  $J = 2$ , and from  $J = 1$  to  $J = 3$ , respectively; hence the decrease of energy in scattered radiation is sometimes due to an increase of the rotational energy of the molecule, the vibrational level remaining unaltered. It is interesting to note that the change in the rotational quantum number in connection with the Raman effect is two, whereas in other spectra, *viz.*, electronic, vibrational or rotational, the change is generally unity and sometimes zero. This is in harmony with the requirements of the quantum mechanical theory of the Raman effect (p. 243). From the separation of the rotational Raman lines it is possible to determine the moment of inertia of a molecule (p. 193); it is important to remember, however, that since  $J$  changes by two units the frequency separation is twice the normal value.

Additional evidence that the Raman spectrum can depict rotational transitions is provided by the observations of Rasetti (1929) that for oxygen gas the alternate rotational Raman lines are missing, corresponding with the symmetry of the molecule and the absence of nuclear spin. Nitrogen, on the other hand, has alternate lines which are strong and weak, since the nuclei possess spin momentum.

**The Q Branch.** It may be seen from Table L. that when the Raman effect is due to a rotational transition there is no vibrational change. On the other hand, when there is a vibrational transition there is no rotational change; the Raman line may then be regarded as a *Q* branch (p. 203). In ordinary spectra there is no *Q* branch unless the molecules have an angular momentum



about the axis joining the nuclei ; in the Raman spectra, however, scattered lines are obtained, which are definitely equivalent to the *Q* branch of a vibrational spectrum, for molecules of all types. For example, the centre of the vibration-rotation spectrum of hydrogen chloride at  $3.4\mu$  is missing (p. 203), but its frequency may be calculated from the position of the rotational lines in this band ; the value is found to be  $2885.4\text{ cm.}^{-1}$ . In the Raman spectrum, studied by Wood and Mecke (1930), of hydrogen chloride excited by the mercury line of wavelength  $4046\text{ \AA}$  a scattered line appears at  $4581.8\text{ \AA}$ , the frequency difference being

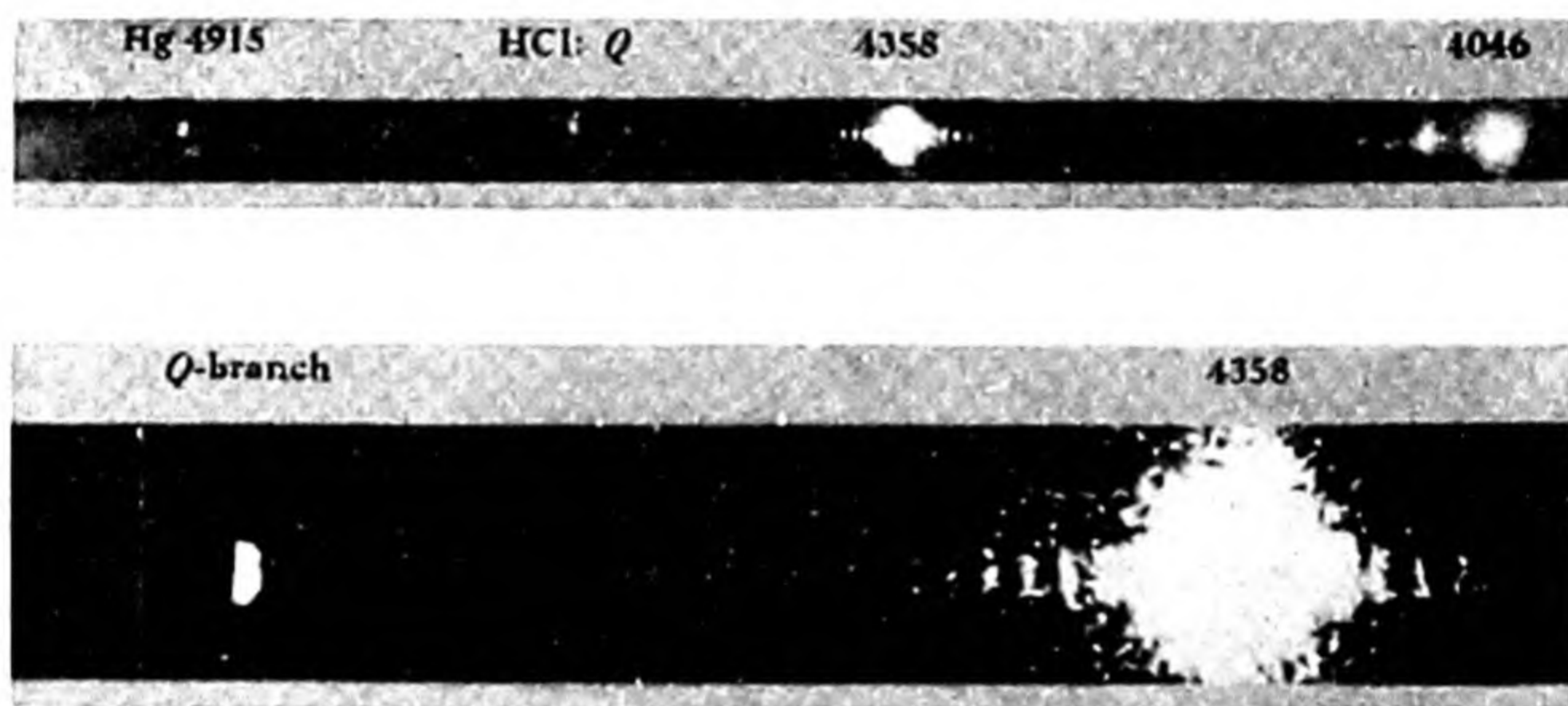


FIG. 20.—Raman spectrum of hydrogen chloride ; the lower photograph, which is an enlargement of a portion of the upper, shows the vibrational Raman line (*Q* branch) stimulated by light of  $4046\text{ \AA}$ , and the rotational lines produced by light of  $4358\text{ \AA}$ . (After Wood and Mecke.)

$2886\text{ cm.}^{-1}$  (Fig. 20) ; this line obviously corresponds with a change of unity in the vibrational quantum number of the molecule with no rotational change, and hence constitutes a *Q* branch. Incidentally Fig. 20 shows the purely rotational Raman lines excited by the mercury line at  $4358\text{ \AA}$  ; from the position of these lines on either side of the incident line it is clear that there is no vibrational transition.

The presence of *Q* branches and the change of two units in the rotational quantum number are examples of a curious characteristic of the Raman effect ; the active frequencies in the scattered light are frequently those which are inactive or “for-



bidden " in ordinary spectra. Mention has already been made of the inactive frequency in the oscillations of the  $\text{CO}_3$  ion ; this vibration is, however, active in the Raman effect. Similar inactive oscillations in the  $\text{NO}_3$  group and in the  $\text{CO}_2$  molecule also become effective in the spectrum of scattered light. It may be seen, therefore, that the Raman effect provides a valuable alternative for, as well as a supplement to, investigations in the infra-red and ultra-violet regions of the spectrum ; it has the great advantage of being stimulated by visible radiation, and it is possible to choose the latter so that the scattered light falls in the region of high sensitivity of a photographic plate. It may be seen from Table XLIX. that the Raman frequency, as it should be, is independent of the frequency of the incident radiation, and so any convenient steady source of light may be used.

**Electronic Raman Transition.** In passing it may be mentioned that Rasetti (1929) has obtained evidence for an electronic transition in the Raman spectrum of nitric oxide.

**Organic Compounds.** An interesting application of the Raman effect has been in connection with organic compounds ; the results bear out the conclusions that Raman transitions are often due to vibrational changes, and the frequency differences correspond to infra-red absorption bands. In the same way as definite infra-red absorption maxima have been ascribed to the vibrations of the atoms constituting definite linkages, so Raman frequencies have been attributed to these vibrations. As is to be anticipated the frequencies obtained by the two methods agree, but those evaluated from the Raman effect are more reliable ; in any case the latter give more accurately the frequency of the centre of the absorption band (Q branch). In general, Raman frequencies fall into four main groups, viz., (a) greater than  $2800\text{ cm}^{-1}$ , (b) between  $2400$  and  $1900\text{ cm}^{-1}$ , (c)  $1800$  to  $1300\text{ cm}^{-1}$ , and (d) below  $1000\text{ cm}^{-1}$ . The highest frequencies are invariably observed with groupings containing a hydrogen atom, the lightness of the atom being responsible for the large value. The substances in the second group generally contain a triple linkage, those in the third a double, and in the fourth a single linkage ; these frequencies are related (p. 253) to the binding forces between the atoms.



**The C — H Linkage.** All aliphatic organic compounds containing the C — H linkage produce a line in the spectrum of the scattered light with a frequency displacement in the close vicinity of  $2980\text{ cm.}^{-1}$ , which is equivalent to a wavelength of  $3.41\mu$ ; this value agrees very well with the position of the absorption maxima in the infra-red ascribed to the oscillations of the atoms in the C — H group. Aromatic compounds; however, with the C — H linkage give a Raman frequency of  $3050\text{ cm.}^{-1}$ , equivalent to a wavelength of  $3.28\mu$ , in excellent agreement with the value deduced from infra-red spectra. The Raman frequency change from aliphatic to aromatic compounds is probably not due to any special feature involved in ring formation, since the characteristic frequency in the latter case is the same as in allyl compounds, and so appears to be connected with the  $=\text{C} - \text{H}$  grouping. Toluene and the xylenes, and their derivatives, produce two lines, amongst others, with frequency displacements of  $2980$  and  $3050\text{ cm.}^{-1}$ , respectively, as these molecules have both aromatic and aliphatic C — H groupings; for some cause, as yet unexplained, benzene itself gives the same two lines, but its derivatives, other than hydrocarbons, do not.

The frequency of  $2980\text{ cm.}^{-1}$  quoted as corresponding to the C — H linkage must not be regarded as a constant in all compounds; it is only to be expected that by changing the groups attached to the carbon atom some variation will result. That this is the case will be seen from the results in Table LI.

TABLE LI

*Characteristic Raman Displacements for the C — H Linkage*

Compound.	$\Delta\nu$ .	Compound.	$\Delta\nu$ .
H·CO·CCl <sub>3</sub> .	2867 cm. <sup>-1</sup>	H·C·Cl <sub>3</sub>	3018 cm. <sup>-1</sup>
H·CO·NH <sub>2</sub> .	2882	H·C <sub>6</sub> H <sub>5</sub>	3050
H·CO·OH .	2951	H·C:N	3213
H·CCl <sub>2</sub> ·CCl <sub>3</sub> .	2985	H·C:CH	3320



Similar variations, generally of the order of 10 per cent. or less, are observed for the Raman frequencies of other groupings.

**Raman Effect and Molecular Structure.** In addition to the C—H frequency, aromatic compounds exhibit Raman frequencies of 997 and 1590  $\text{cm}^{-1}$ ; the former of these is probably due to the C—C linkage, as it occurs in all substances containing this grouping. The frequency of approximately 1600 occurs wherever the C=C grouping is present, for example, 1620  $\text{cm}^{-1}$  in ethylene; hence the 1590  $\text{cm}^{-1}$  frequency in the Raman spectra of aromatic compounds is to be attributed to this linkage. It is opportune to note here that compounds containing trebly linked carbon atoms, *e.g.*, acetylene, have a characteristic frequency of 1960  $\text{cm}^{-1}$ ; the value thus increases with the number of valency bonds involved. Further reference to this matter will be made subsequently. The frequency attributed to the C=O group is 1640 to 1730  $\text{cm}^{-1}$  (compare 1600 for C=C), and 2200  $\text{cm}^{-1}$  for the CN radical. The similarity between this value and that for the C $\equiv$ C linkage (1960  $\text{cm}^{-1}$ ) suggests that the nitrile group has the structure —C $\equiv$ N. The study of the Raman effect can also be used to throw light on other problems of chemical constitution. For example, carbon monoxide gas shows a Raman displacement of 2155  $\text{cm}^{-1}$ ; if this value is compared with the values for —C $\equiv$ N (2200), for —C $\equiv$ C— (1960) and for N $\equiv$ N (2329), the formula C $\equiv$ O is strongly suggested. One of these three bonds is obviously a semi-polar link (p. 18); for further discussion of this subject see pp. 115, 177. The same argument applies to the isocyanide group, which shows characteristic Raman lines with displacements of 2161 and 2146  $\text{cm}^{-1}$ ; it is clear that a triple linkage must be present, and the formula may be represented as — $\overset{+}{\text{N}}\equiv\overset{-}{\text{C}}$ , in agreement with dipole and parachor evidence (pp. 114, 176).

**Raman Effect and Ionisation.** A concentrated aqueous solution of nitric acid has, amongst others, a Raman line for which  $\Delta\nu$  is 1310  $\text{cm}^{-1}$ ; no such frequency is found with sodium nitrate, but a similar line occurs with the nitrite. Organic nitro-compounds, containing the —NO<sub>2</sub> group, all have a line in the scattered spectrum with a frequency displacement of 1400  $\text{cm}^{-1}$ ; hence it



is probable that both sodium nitrite and concentrated nitric acid have an  $-\text{NO}_2$  group. In the former case this is present as an ion, but in the latter it apparently constitutes a portion of the undissociated molecule; this must, presumably, be represented by the formula  $\text{HO}\cdot\text{NO}_2$ . As it happens this formula had previously been suggested for nitric acid in order to account for the results obtained in the nitration of substituted benzene derivatives. It is interesting to note that on dilution by water the Raman line of nitric acid at  $1310\text{ cm.}^{-1}$  gradually fades out and a line at about  $1046\text{ cm.}^{-1}$  displacement appears with increasing intensity (Rao, 1930). The latter is characteristic of the  $\text{NO}_3$  ion, and occurs in the Raman spectrum of crystals and solutions of various nitrates (p. 256). The change in the scattered radiation of nitric acid on dilution is thus evidently due to ionisation.

Krishnamurti (1930) has found that whereas chlorides of metals, which are electrolytes, show no Raman effect in the pure state chlorides of non-metals yield a definite Raman spectrum. This result suggests that the valency forces involved are quite different in the two types of compound; this in harmony with the conclusions reached from a study of X-ray diffraction by crystals and from the electronic theory of valency (Chapter I.). Further evidence of the same nature has been obtained by Woodward (1931), who noted that potassium chloride shows no Raman displacement attributable to the salt, whereas definite lines were observed in mercuric chloride and cyanide solution; these latter are known to be dissociated only to a small extent. Similar evidence for partial dissociation, by the presence of Raman lines, was found in concentrated solutions of sulphuric acid and of potassium hydrogen sulphate. Hydrochloric acid, on the other hand, appears from the Raman spectrum to contain undissociated molecules only in non-aqueous solutions (West and Arthur, 1934).

### STRENGTH OF LINKAGES

Apart from information in connection with molecular structure the determination of characteristic frequencies by means of the Raman effect is yielding interesting results concerning the relative



magnitudes of the forces involved in various chemical valency bonds. Although the atomic oscillations are not truly harmonic the principal Raman frequency provides a very close approximation to the equilibrium vibration frequency ( $\omega_e$ ) of the atoms in the linkage responsible for the particular displacement; if the Raman spectrum contains overtones of the principal line then it is possible, by the application of equation (xviii.), p. 200, to obtain a more accurate idea of the value of  $\omega_e$ . Substituting the reduced mass ( $M$ ) of the group and its equilibrium frequency in equation (xxv.), p. 207, the value of the restoring force ( $f$ ) per cm. displacement of the two parts of the oscillator can be determined. By means of the equation

$$\frac{M}{2} (2\pi a \omega_e c)^2 = h \omega_e c \quad . \quad . \quad . \quad . \quad . \quad (\text{xlvii.})$$

where the left-hand side represents the kinetic energy of the oscillator and the right-hand side the same energy calculated from the quantum theory, it is possible to determine the value of  $a$ , the amplitude of the vibrations. In this way the product of  $f \times a/2$ , which represents the average value of the restoring force, may be evaluated for various linkages. The results given in Table LII. have been calculated in the manner described for linkages of carbon, nitrogen and oxygen, and are quoted from the compilations of Dadieu and Kohlrausch (1930) and of Sidgwick and Bowen (1931).

TABLE LII  
*Mean Restoring Forces and Heats of Dissociation for  
Various Linkages*

Type X—Y	$f \times a/2$ dynes $\times 10^4$	Kilocals.	Type X=Y	$f \times a/2$ dynes $\times 10^4$	Kilocals.	Type X $\equiv$ Y	$f \times a/2$ dynes $\times 10^4$	Kilocals.
C — C	2.08	71	C = C	4.20	125	C $\equiv$ C	6.32	165
C — N	1.98	55	—	—	—	C $\equiv$ N	6.52	183
C — O	2.25	70	C = O	4.44	163	C $\equiv$ O	6.34	235
			O = O	4.18	130	N $\equiv$ N	7.14	170

Two interesting points emerge from an examination of this table: in the first place it is seen that the mean restoring force



appears to depend on the type of linkage and not on the atoms involved in the linkage. This is, however, not the whole truth, since the atoms concerned, carbon, nitrogen and oxygen, have masses and dimensions which are very similar and any relationship holding for them may not necessarily hold for other atoms. The second observation to be made on Table LII. is that the averages of the mean restoring forces for single, double and triple bonds are in the ratio of 1 to 2.02 to 3.04, or approximately 1 : 2 : 3. The force is thus proportional to the number of valencies, that is to the number of electron pairs shared between two atoms; this apparently holds good irrespective of whether the shared electrons are provided equally by both atoms forming the linkage, *e.g.*,  $\text{N} \equiv \text{N}$ , or whether one provides more than the other, *e.g.*,  $\overset{-}{\text{C}} \equiv \overset{+}{\text{O}}$ , as in a semi-polar link. This brings out the important point, already mentioned (p. 33), that there is really no fundamental difference between an ordinary covalency and a semi-polar or co-ordinate covalency.

A compilation of the mean restoring forces for a number of linkages has been made by Kohlrausch (1932); from this it is seen that the values fall into four groups corresponding with the four main groups of Raman frequencies to which reference has previously been made (p. 249). For linkages of the type  $\text{X} - \text{H}$  the mean restoring force, which as a rule decreases with increasing size of  $\text{X}$ , varies from  $4.55 \times 10^{-4}$  for  $\text{H} - \text{H}$  to  $2.52 \times 10^{-4}$  dynes for the  $\text{H} - \text{I}$  link; when carbon is singly linked to elements other than hydrogen the force is  $2.25 \times 10^{-4}$  for  $\text{C} - \text{O}$  to  $1.05 \times 10^{-4}$  dynes for  $\text{C} - \text{I}$ ; the other two groups contain doubly and triply linked elements with mean restoring forces in the vicinity of  $4 \times 10^{-4}$  and  $6 \times 10^{-4}$  dynes, respectively. Although the values within each group are not as constant as those in Table LII. yet the distinction between singly, doubly and triply linked compounds is quite definite. In any group of the periodic table the mean restoring force of the  $\text{C} - \text{X}$  link decreases with increasing atomic weight of  $\text{X}$ ; thus the values for  $\text{C} - \text{Cl}$ ,  $\text{C} - \text{Br}$  and  $\text{C} - \text{I}$  are 1.48, 1.23 and  $1.05 \times 10^{-4}$  dynes, respectively.



**Heats of Dissociation of Linkages.** The value of the mean restoring force may be regarded as a measure of the work necessary to sever the bond involved in any particular linkage; in other words, the magnitude of the force may be expected to be roughly proportional to the heat of dissociation of the bond. That this is the case is shown by the heats of various linkages included in Table LII.; these were determined from thermochemical data by methods similar to that described in connection with the C — H bond (p. 239).

For a given linkage, *e.g.*, C — H, the "reduced mass" is a constant, and so the equilibrium vibration frequency will be proportional to the square root of the restoring force, and hence, approximately, to the heat of dissociation of the linkage. It has been mentioned previously that the Raman frequency, which is approximately equal to the equilibrium oscillation frequency, of the C — H group is 2930, whereas for the = C — H group it is 3050  $\text{cm}^{-1}$ ; the corresponding value when the carbon atom is joined to a neighbouring atom with a triple linkage, *i.e.*,  $\equiv$  C — H, as in acetylene, is 3320  $\text{cm}^{-1}$ . For purposes of comparison it may be repeated here that the equilibrium frequency of the C — H radical, determined from the band spectra of hydrocarbon flames, is 2800  $\text{cm}^{-1}$ . The results indicate that as the number of valency bonds joining the carbon atom of the C — H group to the adjacent C atom increases, so also does the restoring force between the carbon and hydrogen atoms, and the heat of dissociation of the linkage. As already mentioned, the force between the carbon and the other atom to which it is joined also increases with increasing valency; hence it appears probable that the influence of this force is experienced beyond the immediate range of the atoms directly concerned in the linkage. Thus the strong restoring force between the carbon atoms in acetylene causes the force operative between the carbon and hydrogen to be higher than normal; the corresponding equilibrium vibration frequency of the C — H group is larger than if the carbon atoms were joined by single linkages. This example of the influence of the bulk of the molecule on the fundamental oscillations of certain groupings is typical of what must undoubtedly occur in many other instances.



It must be pointed out that the parallelism between the restoring forces and heats of dissociation of linkages can only be approximate: the former are based on  $\omega_e$  and assume harmonic vibrations, whereas the latter apparently also involve the anharmonicity constant  $x$ , as shown by equation (xlii.a). In any case, what has been described as the vibration frequency of a linkage should perhaps be regarded, more accurately, as referring to a mode of vibration of the *molecule*, which is controlled mainly by the C — H force constant. These limitations, however, do not detract appreciably from the importance of the results.

### RAMAN EFFECT IN SALTS

**Nitrates.** The results obtained in the study of the light scattered by solid salts confirm the views already expressed concerning their internal vibrations (p. 242); the oscillation frequencies obtained from the difference between incident and scattered radiations are characteristic of the ions, and not of the molecules of a salt. In confirmation of this statement is the fact that the Raman frequency of solid nitrates, which coincides with the "inactive" frequency (p. 241) of these salts, is almost the same for all the nitrates examined (Grassmann, 1932) as well as for solutions and melts of these salts. The results quoted in Table LIII. (Gerlach, Krishnamurti, 1930), are for the oscillation frequencies calculated from the Raman spectra; the corresponding value for nitrate solutions is  $1045\text{ cm.}^{-1}$  and for a mixture of molten sodium and potassium nitrates it is  $1042\text{ cm.}^{-1}$

TABLE LIII.—*Oscillation Frequencies of Nitrates*

	cm. <sup>-1</sup> .		cm. <sup>-1</sup> .
Lithium nitrate .	1085.8	Calcium nitrate .	1064.3
Sodium nitrate .	1067.5	Strontium nitrate .	1054.4
Potassium nitrate .	1048.4	Barium nitrate .	1046.5
Silver nitrate .	1045.0	Lead nitrate .	1045.0

The smaller the cation and the higher its charge, the greater the oscillation frequency; and hence the restoring force between the oxygen atoms and the nitrogen atom, to the oscillations of which



the usually inactive frequency is supposed to be due (p. 241). It is not improbable, therefore, as already suggested that the cation exerts a distorting action on the anion radical in the space lattice of the crystal.

**Frequency of  $\text{XO}_4$  Group.** The influence of the size and charge of the central atom in ions of the  $\text{XO}_4$  type is shown by the characteristic frequencies given in Table LIV., determined from the Raman spectra of solutions of the compounds concerned. The increasing frequency of oscillation in the chromium series is somewhat unexpected. The value for a solution of telluric acid is included in the Table, but its complete disagreement with the other frequencies serves to show that its structure is not of the  $\text{XO}_4$  type; this confirms the conclusion reached on chemical grounds that  $\text{H}_2\text{TeO}_4 \cdot 2\text{H}_2\text{O}$  should actually be represented as  $\text{Te}(\text{OH})_6$ .

TABLE LIV

*Oscillation Frequencies of  $\text{XO}_4$  Groups in Solution*

	cm. <sup>-1</sup> .		cm. <sup>-1</sup> .		cm. <sup>-1</sup> .
Sodium sulphate	979	Sulphuric acid	989	Sodium chromate	855
Sodium selenate	830	Telluric acid	648	Sodium molybdate	898
		Perchloric acid	937	Sodium tungstate	931

### CONCLUSION

The difficulties involved in the interpretation of the results obtained in the study of various types of band spectra are very great even with comparatively simple molecules, and so the treatment given here can only be regarded as an elementary introduction to certain aspects of the subject. Enough has been said, however, to give the chemist an idea of the lines along which progress is being made and of the conclusions which are likely to be of interest to him.

### REFERENCES

- ANDREWS *et al.* *Phys. Rev.*, 1930, 36, 531; *J. Ind. Eng. Chem.*, 1931, 23, 1282\* ; *J. Chem. Ed.*, 1931, 8, 1133\* ; *J. Chem. Physics*, 1935, 3, 175, 180.  
 BARKER and MEYER. *Trans. Faraday Soc.*, 1929, 25, 912.  
 BARNES *et al.* *Physical Rev.*, 1935, 47, 918.



- BARRATT. *Ann. Reports*, 1926, 23, 304\*.
- BARTHOLOMÉ and TELLER. *Z. physikal. Chem.*, 1932, B19, 366.
- BEUTLER. *Z. physikal. Chem.*, 1934, B27, 287; 1935, B29, 315.
- BIRGE. *Trans. Faraday Soc.*, 1929, 25, 707, 718.
- BIRGE and SPONER. *Phys. Rev.*, 1926, 28, 259.
- BONINO. *Trans. Faraday Soc.*, 1929, 25, 876.
- CONDON. *Phys. Rev.*, 1926, 28, 1182; 1928, 32, 858.
- CZERNY. *Z. Physik*, 1925, 34, 227; 1927, 44, 235; 1927, 45, 470.
- DADIEU. Article in Freudenberg's "Stereochemie," 1932, p. 164\*.
- DADIEU and KOHLRAUSCH. *Ber.*, 1930, 63, 251, 1657; 1931, 64, 358; *Monatsh.*, 1930, 55, 379; 1931, 57, 225, 437, 488; 1932, 61, 369; *Physikal. Z.*, 1932, 33, 165.
- DAMASCHUN. *Z. physikal. Chem.*, 1932, B16, 81.
- DARROW. *Chem. Reviews*, 1928, 5, 451\*.
- DIEKE and HOPFIELD. *Z. Physik*, 1926, 40, 299.
- DUTT. *Proc. Roy. Soc.*, 1932, 137A, 366; 138A, 94.
- ELLIS. *Trans. Faraday Soc.*, 1929, 25, 888; *Phys. Rev.*, 1929, 33, 27; *J. Amer. Chem. Soc.*, 1929, 51, 1384.
- FRANCK *et al.* *Trans. Faraday Soc.*, 1925, 21, 536; *Z. Elektrochem.*, 1930, 36, 581; *Z. physikal. Chem.*, 1932, B18, 88.
- GARNER and LENNARD-JONES. *Trans. Faraday Soc.*, 1929, 25, 611, 942.
- GOODEVE and STEIN. *Ibid.*, 1931, 27, 393.
- GRASSMANN. *Z. Physik*, 1932, 77, 616.
- GRIFFITH and MCKEOWN. "Photo-processes in Gaseous and Liquid Systems," 1929.
- HARDY, BARKER and DENNISON. *Phys. Rev.*, 1932, 42, 279.
- HARKINS *et al.* *J. Amer. Chem. Soc.*, 1931, 53, 2425; 1932, 54, 3929.
- HENRI. *Nature*, 1924, 114, 894; 1930, 125, 202; *Trans. Faraday Soc.*, 1929, 25, 765.
- HERZBERG. *Z. physikal. Chem.*, 1930, B9, 43; 1930, B10, 189; *Z. Physik*, 1930, 61, 604.
- HIBBEN. *Chem. Reviews*, 1936, 18, 1\*.
- IMES. *Astrophys. J.*, 1919, 50, 251.
- JEVONS. "Report on Band Spectra of Diatomic Molecules," 1932\*.
- JOHNSON. *Trans. Faraday Soc.*, 1929, 25, 649.
- KING and BIRGE. *Phys. Rev.*, 1929, 34, 376; *Astrophys. J.*, 1930, 72, 19.
- KOHLRAUSCH. *Physikal. Z.*, 1931, 32, 385; *Z. Elektrochem.*, 1934, 40, 419\*; *Z. physikal. Chem.*, 1933, B20, 217; 1935, B28, 340; "Der Smekal-Raman Effekt," 1931\*.
- KRATZER. *Z. Physik*, 1920, 3, 289, 460; 1921, 4, 476; 1924, 23, 298.
- KRONIG. "Band Spectra and Molecular Structure," 1930\*; "The Optical Basis of the Theory of Valency," 1935\*.
- LANGSETH. *Z. Physik*, 1931, 72, 850; *Nature*, 1931, 128, 225; *Z. physikal. Chem.*, 1934, B27, 100.
- LECOMTE. *Trans. Faraday Soc.*, 1929, 25, 864.
- LOCHTE-HOLTGREVEN and BAWN. *Ibid.*, 1932, 28, 698.
- LOOMIS. *Nature*, 1920, 106, 179; *Astrophys. J.*, 1920, 52, 248.
- MCLENNAN. *Trans. Faraday Soc.*, 1929, 25, 797.
- MECKE *et al.* *Ibid.*, 1929, 25, 936; 1931, 27, 359; *Z. physikal. Chem.*, 1929, B5, 533; *Z. Elektrochem.*, 1930, 36, 589; *Z. Physik*, 1931, 68, 362; *Physikal. Z.*, 1932, 33, 1, 833; "Bandenspektren und ihre Bedeutung für die Chemie," 1929\*; Article in Freudenberg's "Stereochemie," 1932, p. 183\*.
- MEYER and LEVIN. *Phys. Rev.*, 1929, 34, 44.
- MORSE. *Ibid.*, 1929, 34, 57.
- NAUDÉ. *Ibid.*, 1930, 36, 338.



- RABINOWITSCH. *Z. Elektrochem.*, 1931, 37, 91.  
RAMAN. *Trans. Faraday Soc.*, 1929, 25, 781.  
RAMAN and KRISHNAN. *Indian J. Physics*, 1928, 2, 399.  
RAO. *Proc. Roy. Soc.*, 1930, 127A, 279; *Ind. J. Physics*, 1933, 8, 123.  
RAWLINS. *Trans. Faraday Soc.*, 1929, 25, 925.  
RAWLINS and TAYLOR. "Infra-Red Analysis of Molecular Structure," 1929\*.  
RIDEAL. *Trans. Faraday Soc.*, 1929, 25, 921.  
SALANT and SANDOW. *Phys. Rev.*, 1931, 37, 873.  
SCHAEFER and MATOSSI. "Das Ultrarote Spektrum," 1930\*.  
SCHAEFER *et al.* *Z. Physik*, 1926, 39, 648; 1927, 45, 493; 1930, 65, 289; *Trans. Faraday Soc.*, 1929, 25, 841.  
SIRKAR. *Ind. J. Physics*, 1932, 7, 431\*.  
SNOW. *Trans. Faraday Soc.*, 1929, 25, 931.  
SNOW and RIDEAL. *Proc. Roy. Soc.*, 1929, 126A, 355.  
SPONER. *Z. Elektrochem.*, 1928, 34, 483; "Molekülspektren," 1935, Vol. II.\*.  
SUTHERLAND. *Ann. Reports*, 1935, 32, 53\*; "Infra-Red and Raman Spectra," 1935\*.  
TAYLOR, A. M. *Trans. Faraday Soc.*, 1929, 25, 830, 856, 860.  
TAYLOR, H. S. *J. Physical Chem.*, 1930, 34, 2049.  
THOMPSON. *Ann. Reports*, 1933, 30, 56\*.  
TURNER. *Z. Physik*, 1930, 65, 465; 1931, 68, 178.  
UREY. *J. Ind. Eng. Chem.*, 1931, 23, 1241\*.  
VENKATESWARAN and BHAGAVANTAM. *Proc. Roy. Soc.*, 1930, 128A, 252.  
VILLARS. *Chem. Reviews*, 1932, 11, 369\*.  
WEIZEL. "Bandenspektren," 1931\*; *Physikal Z.*, 1933, 34, 425\*.  
WEST and ARTHUR. *J. Chem. Physics*, 1934, 2, 215.  
WOODWARD. *Physikal. Z.*, 1931, 32, 777; *Proc. Roy. Soc.*, 1934, 144A, 129; *Ann. Reports*, 1934, 31, 21\*.

\* Review papers and books, wherein further references are to be found, are marked by an asterisk.



## CHAPTER V

### HOMOGENEOUS GAS REACTIONS

**Homogeneous and Heterogeneous Reactions.** In recent years it has been found that many gas reactions which were at one time considered to be homogeneous are really heterogeneous, and the actual decomposition or combination occurs to a large extent, if not entirely, on the walls of the containing vessel, or on the surface of any suitable solid which may be present. In such cases it is observed that the rate of reaction is markedly increased if the size of the vessel is altered so that the ratio of surface to volume is increased, or if powdered material of which the vessel is made is added so as to increase the surface exposed to the reactants. A number of gas reactions are known, however, for which the rate is independent of the surface area of any solids present and of the enclosing vessel; such processes are definitely homogeneous. On the other hand, there are a number of reactions which are definitely homogeneous, although their velocity *decreases* as the surface to volume ratio is increased: such reactions generally proceed by a chain mechanism (p. 307).

Of the known homogeneous reactions those of the third order presumably require that three molecules should be very close together at one particular instant, and the probability of this occurring is not very great; actually very few termolecular reactions are known. In 1925 only one homogeneous gas reaction of the first order was known definitely, namely, the thermal decomposition of nitrogen pentoxide. Since that date as a result of intensive research a considerable number of such reactions has been discovered. Second order homogeneous gas reactions have been known for some time, and the mechanism of such processes, which appears to be comparatively simple, will be dealt with first.



## THE MECHANISM OF GAS REACTIONS

**Bimolecular Reactions.** For a bimolecular reaction the first possibility suggesting itself is that combination or decomposition occurs whenever there is an impact between two molecules. In practice, however, it is found that the actual rates of bimolecular reactions are very much less than this mechanism would imply. From the kinetic theory it may be shown that for any gas containing one chemical species only, the number of molecules in one cubic centimetre entering into collision per second is  $\sqrt{2}\pi\sigma^2\bar{u}n^2$ ,\* where  $\sigma$  is the "effective," or "collision," diameter,  $\bar{u}$  is the root mean square velocity, and  $n$  is the actual number of molecules in the cubic centimetre. The value of  $\sigma$  may be determined approximately from measurements on the viscosity of gases (Rankine);  $\bar{u}$  can be calculated from the simple kinetic theory equation  $pv = 1/3 mn\bar{u}^2$ ;  $n$  is known from the Avogadro number, and so the number of molecules involved in collisions may be estimated. Consider, for example, the gas hydrogen iodide at 556°K:  $\bar{u}$  is found to be  $3.3 \times 10^4$  cm. per second, and  $\sigma$  is taken by Hinshelwood as  $3.5 \times 10^{-8}$  cm. (Rankine, 1922). This latter value is probably somewhat greater than the true molecular diameter, but it is supposed that molecules do not require to be in actual contact before the mutual forces, which are equivalent to a collision, become operative. If the concentration of the hydrogen iodide gas is 1 gm. mol. per litre, that is  $6.06 \times 10^{23}$  molecules in one litre, then  $n$ , the number per c.c., is  $6.06 \times 10^{20}$ . From these values it follows that the number of molecules colliding per second is about  $6 \times 10^{31}$  in 1 c.c. of gas, or  $6 \times 10^{34}$  molecules per litre. If the thermal decomposition of hydrogen iodide, which is a homogeneous bimolecular reaction, occurred whenever two molecules collided this figure would give the number reacting per second for the concentration specified; the actual value, as found by Bodenstein and by others, is very much less than this, and is in fact about  $2 \times 10^{17}$  molecules decomposing in 1 litre per second. The marked discrepancy indicates quite definitely that only a very

\* A slightly different value is given by some authors, but this does not affect the main argument.







of activation," representing the minimum energy which a molecule must acquire before it can be regarded as being activated.\*

For a bimolecular reaction a collision will only result in chemical reaction if the two molecules between them possess excess energy equal to, or greater than, the heat of activation ( $E$ ) for that

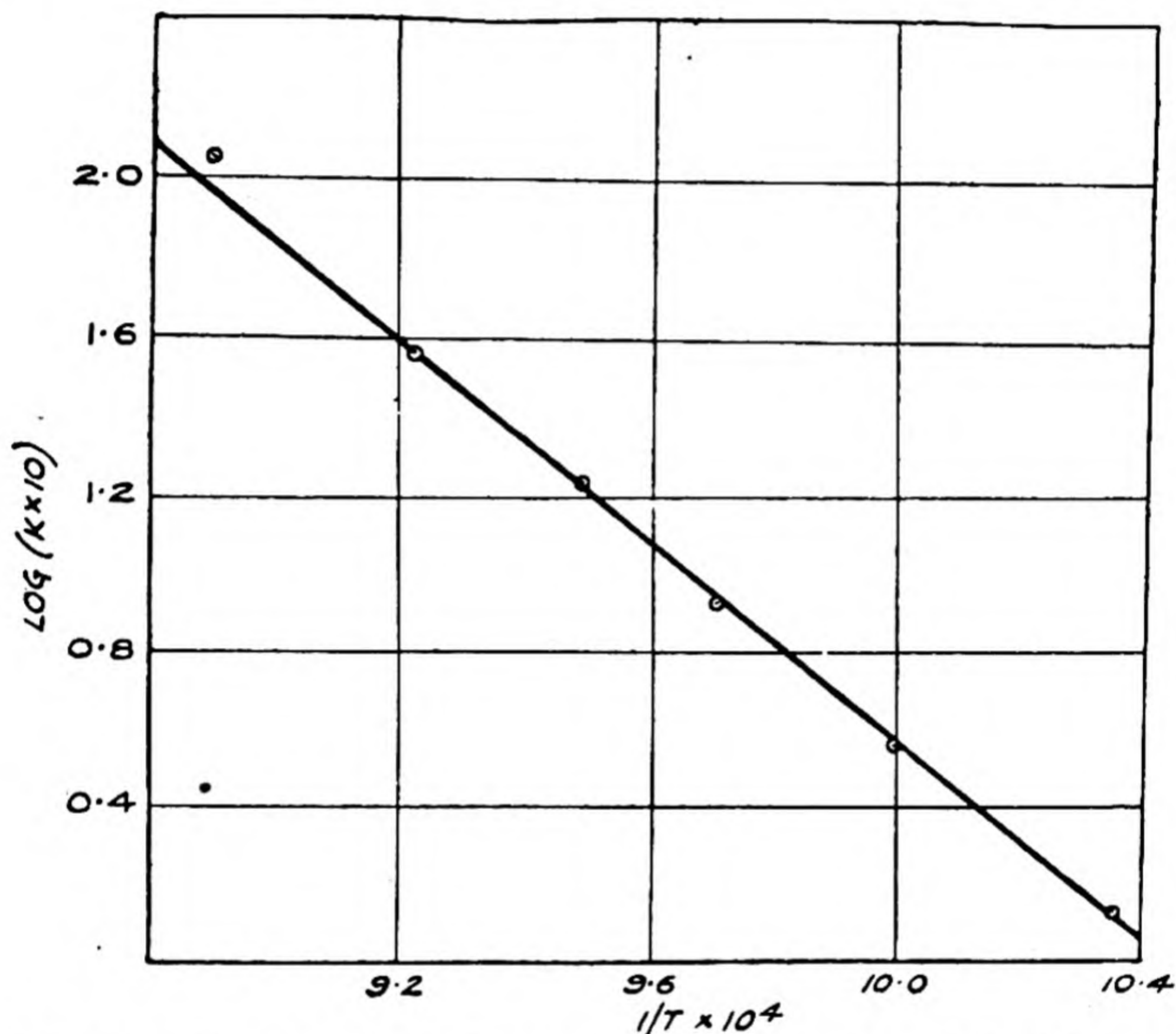


FIG. 21.—The variation of reaction velocity constant ( $k$ ) with temperature in the thermal decomposition of nitrous oxide; the plot of  $\log k$  against the reciprocal of the absolute temperature is a straight line. (After Hinshelwood.)

particular process. It must be emphasised (Hinshelwood, 1927) that the energy of activation is characteristic of a process or reaction and not of a substance; for example, in the decomposition

\* Many writers, *e.g.*, Kassel, Tolman, define the energy of activation as the difference between the energy of an activated molecule and the mean energy of all the molecules; Hinshelwood calls this the "critical increment," and uses the definition of energy of activation employed in this book which Kassel and Tolman call the "critical energy." The differences between the various terms are, however, quite small in comparison with their actual values.



of hydrogen iodide the heat of activation depends on whether the reaction is homogeneous or heterogeneous, and, if the latter, on the nature of the surface (see p. 431).

**Nature of Activation Energy.** The next point to decide is the fraction of the total number of impacts in which the necessary energy of activation is available; before doing so it is essential to consider what is the nature, or type, of the energy required before a molecule can become activated, and so react. If the energy were kinetic energy of translational motion only, the number of molecules possessing the requisite amount for activation would probably be much less than if rotational and vibrational energy also were included. The simplest assumption to make, and one that fits in excellently with the actual results, is that the *only* energy concerned is the translational energy *along the direction of impact*; it should be made clear that it is not the whole of the kinetic energy of the molecule which is supposed to be involved, but the translational component in one direction only, namely, along the line joining the centres of gravity of the colliding molecules. This energy is expressed in terms of the square of the component of the molecular velocity in the appropriate direction, and so for the two molecules concerned in an impact, the total energy, for the purpose under discussion, involves two "square terms," or two "degrees of freedom" only.

As a result of continual impacts of the molecules of a gas upon one another their velocities and energies will not all be the same; at any instant, however, there is a definite probability that a certain number of molecules will have energy in excess of a given amount. By a method similar to that used by Maxwell in developing the Law of Distribution of Molecular Velocities it may be shown that the fraction of the total number of molecules in a gas with energy in excess of  $E$  is equal to  $e^{-E/RT}$ , provided the energy involves only two "square terms." In other words,  $e^{-E/RT}$  represents the probability that in any particular collision the molecules will possess between them at least an amount of energy  $E$ , of the appropriate kind. If the energy concerned in the term  $E$  is of different types, e.g., translational, vibrational and rotational, and so contains more than two "square terms," the number of



collisions involving molecules with the requisite amount of energy is decidedly greater than  $e^{-E/RT}$ ; it will be shown shortly, however, that in bimolecular reactions, at least, the energy terms other than translational need not be included.

**Number of Effective Collisions.** Assuming for the present that the energy of activation of two molecules concerns two "square terms" only, then if  $z$  is the number of molecules in 1 c.c. colliding per second ( $z = \sqrt{2\pi\sigma^2\bar{u}}n^2$ ), the number of these possessing sufficient energy to become activated is  $ze^{-E/RT}$ . If it is assumed that all collisions involving molecules with the necessary energy result in chemical combination, then the reaction velocity is equal to the number of molecules involved in such collisions; that is

$$\frac{dx}{dt} = ze^{-E/RT} \quad \dots \dots \dots (ii.)$$

For a bimolecular reaction the velocity is also proportional to the square of the concentration, or number of molecules in unit volume, of the reacting substance; hence

$$\frac{dx}{dt} = kn^2 \quad \dots \dots \dots (iii.)$$

where  $k$  is the velocity constant, and  $n$  the number of molecules per c.c. It follows then that

$$kn^2 = ze^{-E/RT}$$

and

$$k = (\sqrt{2\pi\sigma^2\bar{u}})e^{-E/RT} \quad \dots \dots \dots (iv.)$$

$$\therefore \ln k = \ln(\sqrt{2\pi\sigma^2\bar{u}}) - E/RT \quad \dots \dots \dots (v.)$$

In the expression  $\sqrt{2\pi\sigma^2\bar{u}}$  the only factor which varies with temperature is the root mean square velocity, but this does not change very greatly, and so may be regarded almost as constant; it is then possible to differentiate equation (v.) with respect to  $T$ , and obtain the following result

$$\frac{d \ln k}{dT} = \frac{E}{RT^2} \quad \dots \dots \dots (vi.)$$

This equation is identical with the Arrhenius equation (i.), although



based on quite different assumptions, and by means of it the heat of activation ( $E$ ) of reacting molecules may be determined.\*

**The Effect of Temperature.** Since the value of  $e^{-E/RT}$  is generally very small it is easy to understand why only a small proportion of the impacts between molecules actually results in chemical decomposition. For example, if  $E$  is 40,000 cal. per gm. mol., a not improbable value, and  $T$  is 500° K., then

$$e^{-40,000/2 \times 500} = 4.25 \times 10^{-18},$$

and only one collision in  $2.4 \times 10^{17}$  will be effective in producing chemical reaction; at a temperature of 1000° K., the value of  $e^{-E/RT}$  is given by

$$e^{-40,000/2 \times 1000} = 2.06 \times 10^{-9}.$$

An increase of temperature thus causes a very rapid increase in the number of molecules possessing the appropriate amount of energy required for reaction to occur; the reaction velocity thus increases very considerably with increasing temperature. In the example quoted the speed of the reaction is increased  $5 \times 10^8$  times when the temperature is raised 500° C. The greater the value of  $E$  the more marked will be the effect of temperature on the rate of reaction.

Incidentally it may be noted that the larger the value of  $E$  the smaller will be the number of fruitful collisions at a given temperature, and so at a constant temperature the greater is  $E$  the smaller should be the reaction velocity. In agreement with this anticipation Hinshelwood has found that if a bimolecular reaction has a heat of activation of about 20,000 cal. per gm. mol. it has a conveniently measurable velocity at 350° K.; if the heat of activation is 40,000 cal. the velocity is measurable at 700° K., and if 60,000 cal. it is estimated that the same speed will only be attained at a temperature of about 1,000° K. This generalisation often permits of a rough determination being made of the energy of activation of a process from the temperature at which the velocity becomes appreciable.

\* If the variation of  $\bar{u}$  with temperature is taken into consideration  $E$  in equation (vi.) is replaced by  $E + \frac{1}{2}RT$ ; except at very high temperatures the additional term may be ignored.



**Calculation of Velocity Constant.** It has already been found that in hydrogen iodide at a concentration of 1 gm. mol. per litre about  $6 \times 10^{34}$  molecules collide per sec. in 1 litre at  $556^\circ \text{K}$ . The number of colliding molecules possessing the necessary energy to permit them to react is, therefore,  $6 \times 10^{34} \times e^{-E/RT}$  in 1 litre per sec. From Bodenstein's observations on the rate of decomposition of hydrogen iodide at various temperatures it is found, by means of equation (vi.), that  $E$  is 44,000 cal. per gm. mol., and so the number of molecules decomposed per sec. is

$$6 \times 10^{34} \times e^{-44,000/2 \times 556} = 3.25 \times 10^{17}.$$

The total number of molecules present in 1 litre is  $6.06 \times 10^{23}$ , that is 1 gm. mol., and so the fraction of 1 gm. mol. reacting in one second when the total concentration is 1 gm. mol. per litre is

$$\frac{3.25 \times 10^{17}}{6.06 \times 10^{23}} = 5.3 \times 10^{-7}.$$

This fraction actually gives the reaction velocity constant,  $k$ , of the decomposition when concentrations are expressed in terms of *gm. mols. per litre*, and the time in seconds; it follows, therefore, that in the decomposition of hydrogen iodide at  $556^\circ \text{K}$ ., the value of  $k$  should be  $5.3 \times 10^{-7}$ . The value obtained experimentally was  $3.5 \times 10^{-7}$ ; considering the magnitudes involved and the uncertainty of the molecular diameter used in calculating the number of colliding molecules (p. 261), the agreement is very good, and lends strong support to the theory developed here, that a bimolecular reaction only occurs as a result of a collision between two molecules possessing energy in excess of a certain amount.

**Calculation of Heat of Activation.** The value of  $k$  calculated in this manner depends on the accuracy of the heat of activation, and a small error in the latter, since it appears in an exponential term, will produce a large effect on the result. An appreciable divergence between this and the experimental quantity may easily be due to an error in  $E$ , rather than to any weakness of the theory. An alternative method of calculation, which does not involve any unreasonable distortion of error, is therefore generally used to compare the experimental results with those to be anticipated from the theory of reaction by the collision of "activated"



molecules. Instead of the measured value of  $E$  being used to calculate  $k$ , the former is determined from the measured reaction velocity, *i.e.*, number of molecules decomposing, since

$$e^{-E/RT} = \frac{\text{number of activated molecules colliding}}{\text{total number of molecules colliding}} \\ = \frac{\text{number of molecules decomposing}}{\text{total number of molecules colliding}} \quad . \quad . \quad (\text{vii.})$$

in a given volume in a given time. The number of molecules decomposing is determined from observations on the progress of the reaction, and the number entering into collisions is calculated by the method already given;  $T$  is taken as the temperature of the observed decomposition, and so  $E$  may be calculated. For the hydrogen iodide decomposition at  $556^\circ \text{K}$ . the value of  $E$  has been determined in this manner as 44,400 cal., whereas the observed value from measurements on the velocity constant at various temperatures is 44,000 cal. per gm. mol.

Two small corrections in the method of calculation have been indicated by Hinshelwood. In the first place the molecules with high energy content which become activated and decompose on collision have a velocity probably greater than the average value ( $\bar{u}$ ) for all the molecules. The number of effective collisions is thus greater than the value already calculated; it is estimated that the number is increased 5 or 6 times because of this factor. In the second place it is possible that a certain definite orientation of the colliding molecules may be necessary for activation and decomposition, even if they have the requisite amount of energy; this will have the effect of reducing the number of collisions resulting in chemical reaction about 2 or 3 times. The combined influence of the two factors mentioned is probably to make the reaction velocity about 2.5 times as great as the value already calculated; that is:

$$\text{Number of molecules reacting per sec. in 1 c.c.} = 2.5 ze^{-E/RT}$$

Applying this correction the value of  $E$  calculated for the hydrogen iodide decomposition is now 45,400 cal., which is not very different from the value determined previously. The corrections discussed are, therefore, not very significant.



The theory that reaction occurs as a result of collision between two activated molecules, with energy in two degrees of freedom, also accounts satisfactorily for the observed reaction velocities in the bimolecular decomposition of nitrogen dioxide, nitrosyl chloride and formaldehyde. The dissociation of nitrous oxide (see p. 302) and of chlorine monoxide are more complex reactions than these, but it appears that the theory of kinetic activation, as described here, can still be applied, at least approximately.

**Origin of Activation Energy.** In Chapter IV. it was implied (see pp. 220, 238) that the dissociation of a molecule resulted when the vibrational energy of a particular linkage exceeded a certain amount; it would thus appear that the "activation" of a molecule involves the raising of its vibrational energy level. It might be reasonably assumed, therefore, that the energy of activation  $E$  is vibrational energy rather than energy of translation. For each vibrational degree of freedom two energy terms, that is two "square terms" are involved, and so in a bimolecular reaction, involving vibrational energy in each of two molecules, the total vibrational energy must be expressed in at least *four* "square terms." The probability that the total energy for two reacting molecules shall be at least equal to  $E$  is now no longer  $e^{-E/RT}$ , except on one condition. The chance of any single molecule concerned in a collision between two molecules having a *vibrational* energy greater than  $E_1$  is  $e^{-E_1/RT}$ , since only two square terms are involved for each molecule, assuming one vibrational degree of freedom. The probability that the other colliding molecule has energy  $E_2$  is  $e^{-E_2/RT}$ . Hence if the sum of  $E_1$  and  $E_2$  is equal to  $E$ , the heat of activation for the reaction, the fraction of the total number of collisions effective in producing activation, and so chemical reaction, is  $e^{-E_1/RT} \times e^{-E_2/RT} = e^{-E/RT}$ . This fraction only applies, therefore, if each separate molecule involved in a collision has to possess at least a definite vibrational energy before it can react.

If no restriction had been made as to the energy content of each molecule concerned in an impact, and the only proviso was that the *sum* of the vibrational energies should be in excess of the amount  $E$ , the total heat of activation, the fraction of



impacts proving effective can be shown to be approximately  $\left(\frac{E}{RT} + 1\right)e^{-E/RT}$ . Since  $E$  may be taken as being on the average about 40,000 calories, and  $T$  may be 700–1,000° K., the value of this fraction is found to be 20 to 30 times  $e^{-E/RT}$ . The rates of bimolecular reactions would, on this theory, be 20 to 30 times the value calculated on the assumption that the probability of reaction occurring in a collision is  $e^{-E/RT}$  only, and the "calculated" and "observed" values of the heat of activation would not be in as good agreement as has been found. It is fairly certain, therefore, that if the energy of activation of a molecule has to be vibrational energy, then it is not a sufficient condition for activation merely to state that the sum of the separate vibrational energies of two colliding molecules must be in excess of the amount  $E$ . If the further restriction is applied, as already shown, that each colliding molecule must have a definite vibrational energy content, then the conclusion reached concerning the number of effective collisions is, as already shown, exactly the same as that arrived at on the assumption that the energy of the reacting molecules is translational, no restriction being made as to the amount supplied by each colliding molecule.

At the present time there appears to be no means of deciding between the two possibilities concerning the origin of the energy of activation; probably most authors favour the view that the energy is originally translational along the direction of impact, as this is the simpler of the two concepts leading to the probability  $e^{-E/RT}$  as the chance of reaction occurring at an impact. According to this theory the mechanism of activation would be that the excess translational energy of the colliding molecules is converted at the moment of impact into vibrational energy (see Franck and Eucken, 1933); the molecules now exist in high vibrational levels and so are regarded as "activated" and ready to decompose or react. Activation, therefore, is supposed to occur as a result of the impact and the re-distribution of energy.

**Two Reacting Substances.** The reactions considered hitherto involve one reacting substance only, but the theory can be extended to apply to a bimolecular reaction between two different



kinds of molecules. The number of collisions between two unlike molecules is given by the expression  $\sigma^2 n_1 n_2 \{8\pi RT(1/m_1 + 1/m_2)\}^{1/2}$ , where  $\sigma$  is the sum of the effective radii of the two kinds of molecules,  $n_1$  and  $n_2$  are the numbers of each kind in unit volume (1 c.c.), and  $m_1$  and  $m_2$  are their respective molecular weights. The number of molecules of each kind reacting in one second per c.c. is then obtained on multiplying this quantity by the probability,  $e^{-E/RT}$ , that any collision will involve two molecules with the required amount of energy in excess of the average. Alternatively, if the reaction velocity constant is known,  $E$  may be calculated and compared with the observed value from the temperature coefficient. The combination of hydrogen and iodine vapour is a bimolecular process, and the data obtained in the study of this reaction may be utilised to test the theory. At  $700^\circ \text{K.}$  the observed value of the velocity constant, with concentrations in gm. mols. per litre per second is  $6.4 \times 10^{-2}$ . The value of  $E$  calculated, taking  $\sigma$  as approximately  $2 \times 10^{-8} \text{ cm.}$ , is about 40,500 cal. per gm. mol., whereas the value determined from the temperature coefficient of the reaction velocity by means of equation (vi.) is 40,000 cal. The agreement is again good, and so it may be taken that the theory of reaction as a result of a collision between molecules possessing between them the energy required for activation is also applicable to a bimolecular reaction between two different substances.

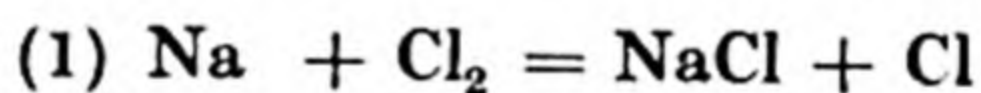
Hinshelwood and Clusius (1930) studied the thermal decomposition of diethyl and *iso*-propyl ethers and acetaldehyde when catalysed by iodine; the observed velocities were in good agreement with those calculated on the basis of the views described above. Similarly, the observed rate of thermal decomposition of ethylene di-iodide is very close to that calculated on the assumption that the rate-determining step is the reaction between the iodide and iodine atoms (Arnold and Kistiakowsky, 1933).

**Heat of Activation and Reaction Velocity.** According to the theory developed the rate of any bimolecular reaction should be proportional to the number of molecules colliding and to the term  $e^{-E/RT}$ . The former quantity depends on the diameter, speed and concentration of the molecules; since molecular diameters

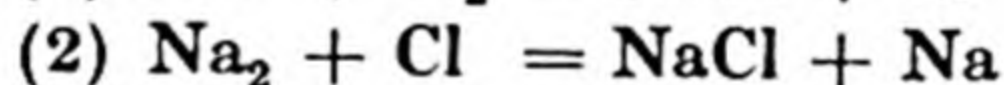


and velocities are all of the same order, then for two gases at the same concentration the number of molecules taking part in collisions is almost the same. The relative rates of two bimolecular reactions should thus depend only on the relative values of  $e^{-E/RT}$ .

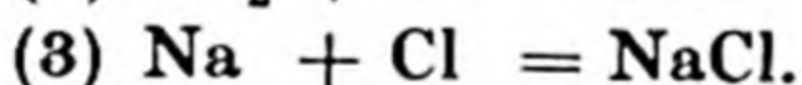
**Atomic Reactions.** Although in most bimolecular processes reaction only occurs between suitably activated molecules, there are a number of reactions, studied by Polanyi and his collaborators (1928 *et seq.*), in which a chemical change results at *every* collision; in other words, the energy of activation of the process is zero. These reactions all involve an atom as one reactant and have consequently been called "atomic reactions"; they have been studied by the ingenious methods of "highly dilute" and "diffusion" flames, on account of the high reaction rates. The reacting gases are allowed to mix at very low pressures (*circa* 0.001 mm.), sometimes in the presence of an inert gas, and the flame produced is due to a chemiluminescent stage in the processes which occur. From an examination of the distribution of solid produced in the process along the walls of the reaction tube and the variation of light intensity it is possible to study the rates of the various chemical changes. When sodium vapour, containing Na and Na<sub>2</sub> molecules, is mixed with chlorine, the reactions are



followed by



and



Reaction (2) is responsible for the light produced, as this is the only process in which sufficient energy is evolved to excite the resulting sodium atom to the state in which it emits the D lines. Both the reactions (1) and (2) appear to be without inertia: that is to say, the reactions take place at every collision and no energy of activation is required. The third reaction, in which atoms of chlorine and sodium are involved, occurs only at about one collision in 10,000; the reason for this will appear later (p. 284). It has also been found that in the reactions between sodium atoms and iodine, hydrogen chloride, bromide and iodide, and mercuric and mercurous chlorides a chemical change probably occurs at every collision; when the reaction is exothermic the energy of



activation is zero, but in endothermic processes the activation energy is equal to the heat absorbed in the reaction. Similar conclusions have been reached from a study of the reaction of potassium atoms with hydrogen halides.

That processes involving atoms are not always without inertia, however, has been shown by von Hartel and Polanyi (1932) in their studies of the reactions of sodium atoms with alkyl and aryl halides; although no activation is required with methyl iodide, increasing amounts are necessary with the bromide, chloride and fluoride. Benzyl chloride reacts with sodium atoms at every collision, but with most other chlorides only one collision in about 10,000 leads to chemical reaction; the energies of activation are not large—5,000 to 10,000 cal.—but they are none the less definite. There are also a number of reactions, *e.g.*, between hydrogen atoms and hydrogen chloride, and between hydrogen molecules and chlorine, bromine, iodine or oxygen atoms, which involve an energy of activation. From a study of atomic reactions it may be concluded that they are not all without inertia, but in those cases in which an activation energy is required the value is generally small in comparison with reactions involving two molecules. It will be seen later (p. 284) that reactions between two atoms belong to a quite different category.

**Abnormal Reactions.** The simple theory of reaction resulting from all activated collisions, whatever the value of the energy of activation, certainly applies in the cases already quoted, but it must be regarded as an ideal only approached in a limited number of instances. The bimolecular polymerisation of ethylene occurs at only one in about 2,000 collisions between *activated* molecules (Pease, 1931), and the polymerisation of 1, 3-butadiene at 1 in 10,000 activated collisions (Vaughan, 1932); the discrepancy in the ethylene-hydrogen reaction is much smaller, since only one-tenth of the collisions involving activated molecules result in reaction (Pease, 1932). In an "ideal" bimolecular reaction the energy of activation always brings about reaction, but in the cases cited above Vaughan considers that in many collisions the energy is re-distributed in the resulting complex; on the next collision the excess energy is removed and the mole-



cules are stabilised, so that no decomposition results. On the other hand, the thermal decomposition of ozone and the reaction between ozone and nitrogen pentoxide are both mainly bimolecular, but the reaction rates are markedly in excess of those calculated on the basis of the simple theory. It is probable that in these reactions a chain mechanism may be involved (p. 302) so that they must be regarded as being in a different category.

**The Probability Factor.** The velocity constant of an "ideal" bimolecular reaction of any type may be expressed by a generalised form of equation (iv.), namely  $k = Ze^{-E/RT}$ , where  $Z$ , called the "collision number," represents the number of collisions per sec. when the gas contains one molecule of each reactant per c.c. In order to account for the fact that certain reactions, such as those just considered, deviate from what may be regarded as ideal behaviour, a probability factor  $P$  is introduced, thus  $k = PZe^{-E/RT}$ , so as to represent the fraction of the activated molecules which actually react on collision. The deviations of  $P$  from unity, which are often quite considerable, have been attributed to such factors as the necessity for the molecules to be correctly orientated, as already mentioned, or for them to be in the correct "phase" on collision. According to Hinshelwood and Winkler (1936), such factors might easily account for  $P$  being as small as  $10^{-4}$  or  $10^{-5}$ , which is of the order found in the polymerisation of 1, 3-butadiene (*vide supra*), and in other similar processes.

A new point of view in connection with the interpretation of the probability factor has been opened up by Eyring (1935) and by Polanyi (1935), following on the earlier work of Tolman (1927), Pelzer and Wigner (1932), and others, in the so-called "transition state" or "activated complex" theory of reaction velocity. This theory develops in an explicit manner the view, which has been long held in a general way, that the first stage in a chemical reaction is the union of the reacting molecules to form an activated complex which subsequently decomposes into the resultants. The activated complex is supposed to resemble an ordinary molecule, except in the respect that it has an additional translational degree of freedom in the direction of decomposition. In the formation of the complex from two molecules, the six (three



for each molecule) degrees of translational and six (three for each molecule) of rotational energy, originally present in the reacting molecules, are reduced to four of translation and three of rotation in the activated complex; the remaining five must be converted into vibrational degrees of freedom. The reluctance for the energy of the molecule to be transferred in this manner is the cause of the deviation of the factor  $P$  from unity; it may therefore be regarded as representing the probability of the formation of the complex when two molecules possessing the necessary energy of activation collide. When the reactants are relatively simple, for example containing only one or two atoms per molecule, the initial number of rotational degrees of freedom is smaller than six, and the probability of the formation of the activated complex approaches unity. This appears to be in general agreement with experimental observations. It may be remarked that the reluctance of the energy to be transferred is probably to be regarded as another way of considering the phase and orientation factors mentioned above: the activated complex and collision theories merely provide different angles from which the same problem may be examined.

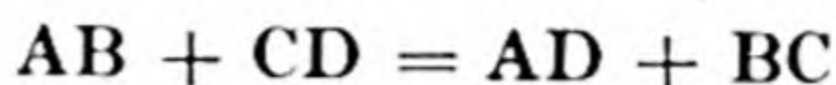
**Theoretical Calculation of Reaction Velocities.** By applying the concept of "partition functions" \* to the activated complex theory it is possible, by making various assumptions, to calculate approximate values of the quantity  $PZ$  from a knowledge of the moments of inertia and vibration frequencies of the reacting molecules and of the hypothetical complex. In certain instances, further, it has been shown by Eyring and Polanyi (1931), whose work is based on the earlier treatment of London (1929), Langer (1929) and Villars (1930), that the activation energy of a reaction, which represents the difference in potential energy of the activated complex and of the reactants, can be calculated. The remarkable situation has therefore been reached wherein it is possible, in a limited number of cases, to calculate reaction velocities theoretically from a knowledge of the physical properties of the molecules concerned. The treatment is still highly approximate, but it

\* The subject is treated in "Recent Advances in General Chemistry," Chapter II., and applied to the activated complex theory in Chapter VII.

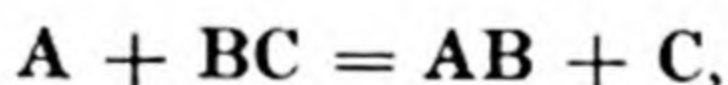


nevertheless marks an important advance, and a brief account will be given of the principles involved in the calculation of activation energies.

Imagine two molecules AB and CD, which can react according to the equation



approaching one another; if the molecules AB and CD are vibrating with sufficient vigour, then it is possible that at the instant of collision the atoms A and B, and C and D are so far apart that it is just as easy for A to combine with D, and B with C, as it is for the original molecules to be re-formed. The minimum total potential energy of the system for this exchange to occur may be regarded as the energy of activation of the reaction; if the reactants have less than this amount of energy then the interchange of partners cannot occur and the reaction will not take place. The variation of the potential energy of a molecule with the distance apart of its constituent nuclei is given approximately by the appropriate Morse equation (p. 216), but this only applies to individual molecules and does not allow for interaction resulting from the mutual action of two different molecules. The necessary allowance is made, however, by the use of the equations proposed by London (1929) for the total potential energy of a system consisting of three or four atoms; in the former case, which can be applied to a reaction of the type



the formula may be written

$$E = A + B + C + \{0.5[(\alpha - \beta)^2 + (\alpha - \gamma)^2 + (\beta - \gamma)^2]\}^{0.5}. \text{ (viii.)}$$

where  $E$  is the total energy of the system, and  $A + \alpha$ ,  $B + \beta$  and  $C + \gamma$  represent the potential energies of the three possible pairs BC, AB and AC, in the absence of the third atom. These potential energy terms are divided into two parts, viz.,  $A$ ,  $B$  and  $C$ , and  $\alpha$ ,  $\beta$  and  $\gamma$ , respectively; the former of these represent the Coulomb, or electrostatic, energy and the latter the interchange, or resonance, energy (p. 61), and although the sum of the two kinds of energy can be determined from spectroscopic data and



the Morse equation, there is no method known for obtaining the two terms separately except in the very simplest cases. As London's equation (viii.) cannot be applied unless the two energy quantities are known, certain assumptions have to be made; by analogy with the values calculated for the hydrogen molecule by the method of Heitler and London (p. 60) it is assumed that the Coulomb energy is only a small fraction of the total. At one time the Coulomb energy was assumed to be as little as 3.5 per cent. of the total, but at present 14 per cent. is the proportion generally assumed. It is clear that this procedure can only be regarded as approximate, but it is the only method at present available.

By means of the Morse curves for the three pairs BC, AB and AC and equation (viii.) it is now possible to calculate, at least approximately, the value of  $E$ , the total potential energy of the system, for various separations of the three atoms involved. The subsequent treatment is simplified by making use of the fact that the energy has been found to be least when the three atoms are in a straight line; the distances apart of the nuclei in any two of the pairs, say AB and BC, then determines the third distance, so that the total energy can be plotted on an ordinary rectangular diagram with the distances between B and C as abscissæ and between A and B as ordinates. When this diagram is completed for a large number of possible configurations of the three atoms A, B and C it is seen that on joining points for which the energy is the same a series of energy contour lines is obtained (Fig. 22). These contours, as a general rule, show two valleys at right angles, parallel to the axes of reference and joined by a pass in the region of the shaded portion of Fig. 22; it is the height of this "energy pass" which gives the energy of activation of the reaction. If the atom A is supposed to be brought up from infinity towards the molecule BC, the distance apart of the nuclei in the latter remaining constant at their normal value, then the potential energy increases gradually, as is seen by following the path in the direction of the arrows. As A approaches BC closely the nuclei of the latter are forced apart somewhat, if the potential energy of the system is to remain a minimum, and when the top of the energy pass is reached the three atoms A, B and C are so



related in position that it is just as easy for B to unite with A as it is for it to remain with C; if the former eventuality results the potential energy of the system, now  $AB + C$ , follows the second valley, as shown in the figure. It will be seen, therefore, that in

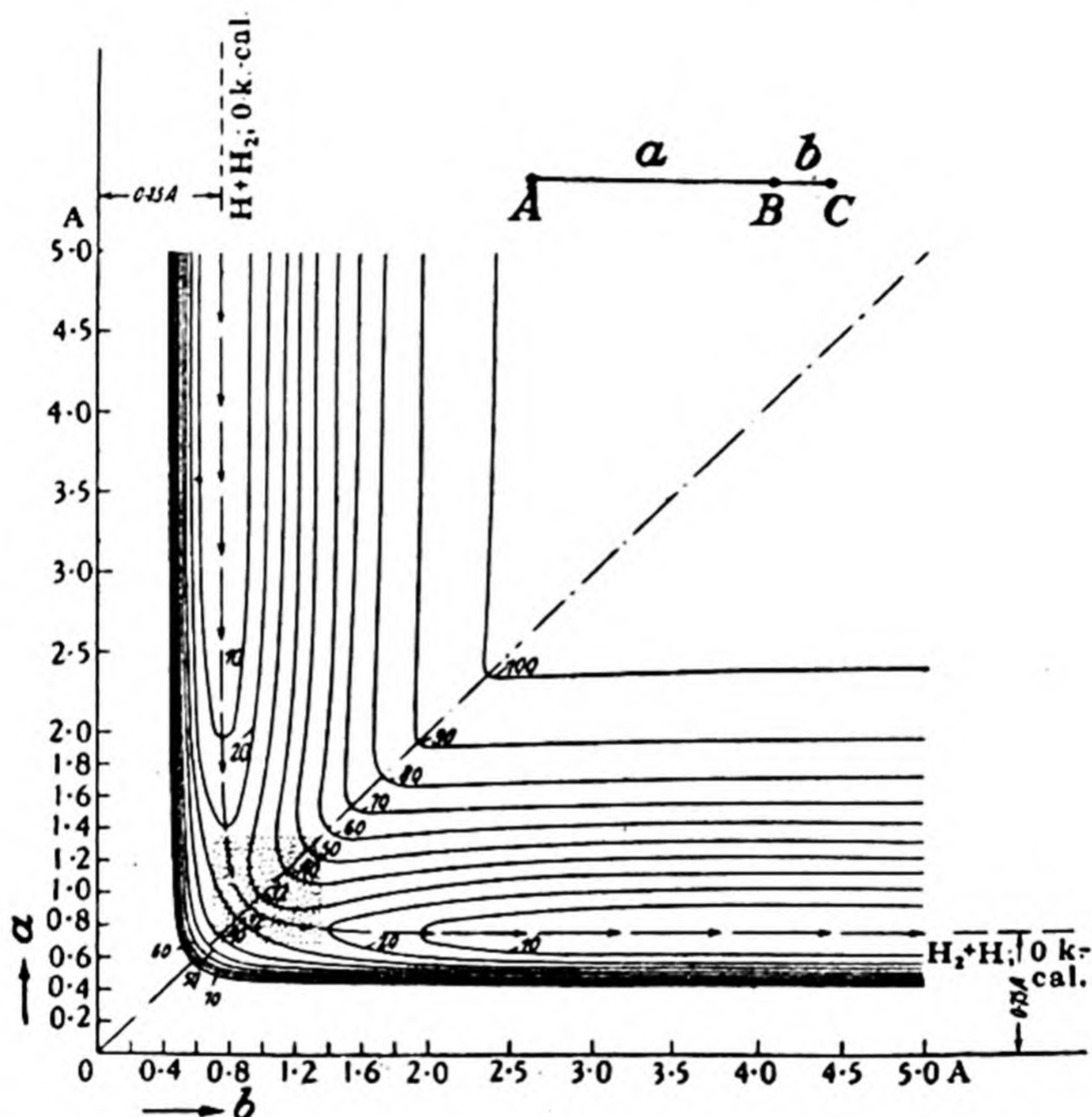


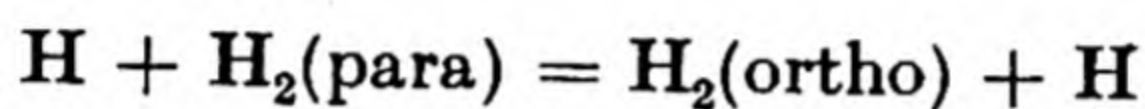
FIG. 22.—Potential energy contours for the reaction  $A + BC = AB + C$ , in this case  $H + p\text{-}H_2 = o\text{-}H_2 + H$ . (After Polanyi and Eyring, and Farkas and Farkas.)

order for A and BC to change over into  $AB + C$  the system must acquire a minimum potential energy represented by the height of the top of the energy pass; if the energy is less than this value then it is not possible to proceed from the valley representing  $BC + A$  to the one at right angles representing  $AB + C$ , and so



the reaction cannot occur. In this way it is possible to calculate the energy of activation for a process of the type under discussion by the aid of spectroscopic data ; the same method can be applied to a system involving two more complicated molecules, but equation (viii.) assumes a more complex form.

When using this method to calculate energy of activation it is not necessary actually to plot the energy contour diagram, as the height of the energy pass, or " saddle " as it is sometimes called, may be calculated by the appropriate mathematical expression of the condition in equation (viii.). In this way Eyring and his collaborators (1932, *et seq.*), and others, have calculated the activation energies for a number of reactions. The process



has probably been studied more fully than any other in the way described, and Fig. 22 refers to this reaction, although the energy values quoted against the contours must be taken as empirical. The latest calculations of the energy of activation give a value of 7,600 cal. (Hirschfelder, Eyring and Topley, 1936), which is in excellent agreement with the experimental result, about 7,000 cal. at ordinary temperatures (Geib and Harteck, 1931).

In most instances it is not possible, however, to make a satisfactory comparison between observed and calculated activation energies ; the division of the potential energy of a molecule into Coulomb and exchange energy cannot yet be estimated with any degree of accuracy, the Morse equation may not represent accurately the variation of potential energy with nuclear separation and there may be other factors involved not yet fully understood. Further, the application of quantum mechanics, which deals with probabilities, shows that there is a definite, although in many cases small, probability (Langer, 1929) that a reaction can occur without the colliding molecules acquiring the energy necessary to bring them to the top of the pass ; in other words, the molecules can " tunnel " through the energy mountain, and so change from one valley to the other. The reactions for which it is at present possible to make a rough estimate of the energy of activation are those not easily studied experimentally, and for

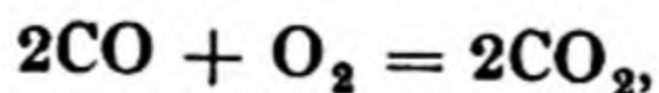


the time being it is only possible to judge the value of the treatment by its qualitative results ; these are undoubtedly interesting and serve to confirm the general ideas involved. For example, Eyring has shown that the reaction of hydrogen and molecular iodine should occur more readily, that is with a lower energy of activation, than the reaction involving iodine atoms ; with the other halogens, however, the reactions with atoms should be preferred. This somewhat surprising conclusion is in agreement with the experimental observations. The theoretical treatment also indicates that bimolecular reactions involving an atom as one of the reactants should have very small activation energies ; this is in agreement with the experimental results on "atomic reactions" of Polanyi and his collaborators (p. 272). It will be seen, therefore, that these calculations of the energy of activation, although in their preliminary stages, mark a definite step forward in the theoretical study of chemical reactions.

### TERMOLECULAR REACTIONS

The occurrence of a reaction of the third order requires that three molecules should either collide simultaneously, or at least that they should come so close together as to be equivalent to a collision, as far as the rearrangement of energy is concerned. The probability of such a ternary impact at ordinary temperatures and pressures is quite small, and hence unless the energy of activation is correspondingly low, so that a large proportion of the impacts results in chemical change, the reaction velocity is likely to be immeasurably slow. It may be concluded, therefore, that if termolecular reactions of reasonable speed are observed the heat of activation is comparatively small.

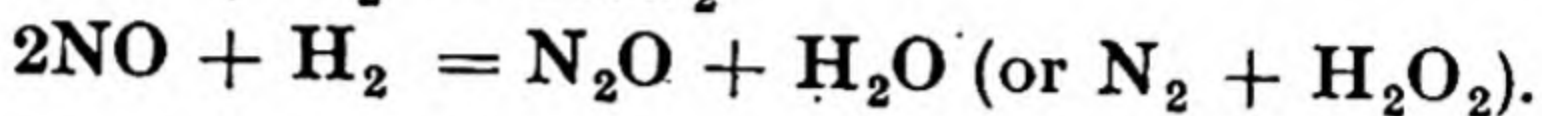
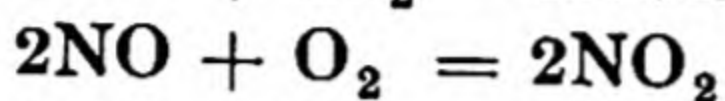
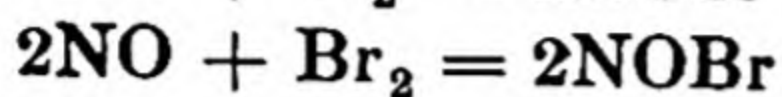
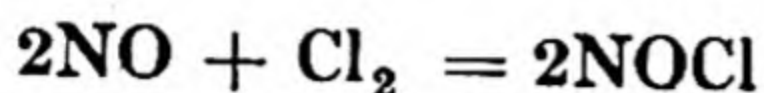
Hitherto only four definite homogeneous reactions of the third order have been discovered ; many processes which appear to be termolecular, *e.g.*,



are probably heterogeneous, or else only occur in the presence of moisture which acts as an intermediate, or catalyst, in a series of



bimolecular stages. The following reactions studied by Trautz (1914, 1918), Bodenstein (1922), Hinshelwood (1926) and others are definitely termolecular :



The reaction between nitric oxide and oxygen, as is well known, occurs at ordinary temperatures, although the velocity constant, in gm. mols. per litre per second, is of the order of  $10^{-6}$ ; curiously enough the speed of the reaction *decreases* somewhat with increasing temperature. The decrease in reaction velocity as the temperature is raised may be connected with the fact that as the speeds of the molecules are increased the chances of two molecules being within attractive range of one another when a third approaches is diminished; the number of ternary collisions thus probably decreases as the temperature is increased. If this decrease is relatively greater than the increase in the fraction of the collisions which are effective in producing chemical decomposition (*i.e.*,  $e^{-E/RT}$ ) the velocity of the reaction will decrease at higher temperatures. Kassel (1931) has made an attempt to calculate the number of triple collisions in an imperfect gas on the basis of the kinetic theory; he found that at low temperatures the number of such collisions might decrease with increasing temperature, but at high temperatures a more normal behaviour is to be anticipated. By applying the activated complex theory (p. 274) Gershinowitz and Eyring (1935) have shown that for a termolecular reaction the velocity constant might be expected to have approximately the form  $k = (Ae^{-E/RT})/T^{7/2}$ , where  $A$  is presumably the equivalent of the  $PZ$  terms in the equation for bimolecular reactions. It follows, therefore, that if  $E$  is small or zero, the reaction velocity will decrease as the temperature is raised; for intermediate values of the energy of activation, however, the velocity will at first increase with temperature and then decrease.

**Ternary Collisions.** An approximate treatment has been developed by Bodenstein and by Hinshelwood along the following



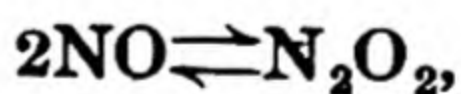
lines: Bodenstein makes the reasonable assumption that the chance of an oxygen molecule hitting two nitric oxide molecules in contact with one another bears the same ratio to the chance that it will hit one molecule as a molecular diameter bears to a mean free path. The ratio of ternary to binary collisions is thus  $10^{-8}$  (the molecular diameter) to  $10^{-5}$  (the mean free path under normal conditions), that is as 1 to 1,000, approximately. With a termolecular reaction the question of orientation of the molecules is much more important than in one of the second order, and it is very probable that only one-tenth of the ternary collisions could be effective even if the molecules had the necessary energy for them to become activated; hence the number of ternary collisions to be considered is only one ten-thousandth part of the number of binary impacts under the same condition. For the reaction of oxygen at  $\frac{1}{2}$  atm. pressure with nitric oxide at  $\frac{2}{3}$  atm. at  $0^{\circ}$  C. the number of binary collisions per second may be calculated as  $3 \times 10^{28}$  per c.c.; hence the number of ternary collisions to be considered is  $3 \times 10^{24}$ . From Bodenstein's experiments it is found that  $7 \times 10^{19}$  molecules actually react in one c.c. per second, and so the ratio of the number of molecules reacting to the number involved in collisions when suitably oriented is about  $10^{-4}$  to  $10^{-5}$ . In a ternary process the number of "square terms" included in the energy of the molecules available for activation must be greater than two; hence the simple probability of effective impact, viz.,  $e^{-E/RT}$ , cannot apply in this case. As a rough approximation, however, this may be put equal to  $10^{-4}$ — $10^{-5}$ , and hence  $E$  evaluated as 5,000—7,000 cal.; as expected, therefore, the heat of activation, and consequently the temperature coefficient of the reaction, must be quite small. The same conclusion must be reached in connection with the termolecular reactions resulting in the formation of nitrosyl chloride and bromide; in these cases the temperature coefficients are actually found to be positive, but quite small.

By applying the activated-complex method to the experimental results Gershinowitz and Eyring (1935) have concluded that the reaction between nitric oxide and oxygen requires no energy of activation, whereas that with chlorine necessitates 4,780 cal.

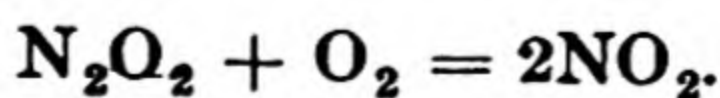


The data for the nitric oxide-bromine reaction are insufficient for exact calculations to be made, but the energy of activation is apparently less than for the corresponding process involving chlorine. The reaction between nitric oxide and hydrogen requires an apparent activation of 47,000 cal. (Hinshelwood and Mitchell, 1936); this is a surprisingly high value for a termolecular reaction, but the kinetics can be accounted for on the assumption that the process mainly involves *binary* collisions between complexes, such as  $(\text{NO})_2$  and  $(\text{NO})(\text{H}_2)$ , and simple molecules,  $\text{H}_2$  and  $\text{NO}$ , respectively.

**Reaction Mechanism.** It may be significant, as Hinshelwood points out, that the four known termolecular reactions all involve two molecules of *nitric oxide*; this may be purely coincidence, or it may be that the "duration of impact" is greater in collisions between two nitric oxide molecules than between other molecules, so that there is more chance of a third molecule, *e.g.*, oxygen, chlorine, bromine or hydrogen, arriving in time to produce a ternary encounter. It is interesting to speculate as to how far the fact that nitric oxide has an odd number of electrons, and is consequently exceptional in many ways, may be connected with it being involved in homogeneous termolecular reactions. Such a substance might be expected to form associated molecules, in which the connection could be either chemical or physical; any association of this type would increase the "duration of impact" between two nitric oxide molecules, and so favour ternary collisions. The extreme case of the extension of this period of impact would be the formation, as Trautz has suggested, of an  $\text{N}_2\text{O}_2$  molecule; the reaction involving nitric oxide and oxygen, for example, might occur in two stages, thus (a) a reversible stage involving a rapid establishment of equilibrium



followed by (b) a slow bimolecular reaction



The speed of the complete process is determined by the second stage, but the whole reaction will appear to be of the third order,



since the concentration of  $\text{N}_2\text{O}_2$  is proportional to the square of that of the  $\text{NO}$  molecules ; that is

$$\frac{d[\text{NO}_2]}{dt} = k_1[\text{N}_2\text{O}_2][\text{O}_2]$$

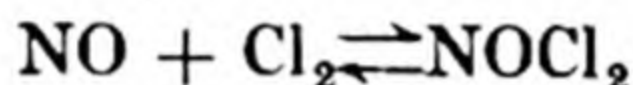
for reaction (b), and

$$\frac{[\text{N}_2\text{O}_2]}{[\text{NO}]^2} = k_2$$

from the equilibrium (a), and so

$$\frac{d[\text{NO}_2]}{dt} = k[\text{NO}]^2[\text{O}_2].$$

An alternative mechanism has been suggested for the reaction between nitric oxide and chlorine, according to which  $\text{NOCl}_2$  is formed as an intermediate product ; thus a rapid equilibrium



is followed by a slow reaction



It is very probable that there is no fundamental difference between the mechanism which implies the formation of an intermediate compound and the one suggesting a physical association ; in any case both views really imply a ternary impact, with the additional suggestion that two of the three molecules are specially attracted to one another. A great deal of further study, including a search for new ternary homogeneous reactions, is required before the exact mechanism of such processes is definitely elucidated. For the present, however, it is reasonable to accept for such reactions an extension of the idea of activation, as a result of a collision of molecules with the appropriate amounts of kinetic energy, developed for bimolecular processes.

### THREE-BODY COLLISIONS

**Recombination of Atoms.** Since the heat of activation of many atomic reactions has been found to be very small or zero (p. 272), it might be anticipated that the combination of two atoms, *e.g.*, of hydrogen, nitrogen or a halogen, to form a molecule



would take place so readily that union would result at every collision. In actual practice this is not the case, and the rate of combination is unexpectedly low. The discrepancy has been explained in the following manner (Herzfeld, 1922; Born and Franck, 1925): whenever two atoms unite the energy content of the resulting molecule will include both the energy of the original atoms as well as the heat of reaction. If the molecule cannot be relieved of its excess energy within a very short interval of time, either by collision with another molecule of any kind or else by impact with the walls of the containing vessel, it will dissociate again into its constituent atoms. A reaction of this type can, therefore, only occur as the result of a three-body collision ("dreierstoss"), viz.,

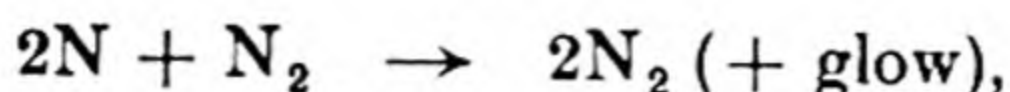


where A represents the reacting atoms, and X is either the wall or any molecule able to remove excess energy from the  $A_2$  molecule. Apart from the wall reaction the process must consequently be regarded as kinetically termolecular, and hence it is obvious that not every collision between two atoms will result in combination. The same three-body collision is necessary in any reaction of the same type, where the resultant molecule carries a large excess of energy and is liable to dissociate unless relieved of this excess.

Bodenstein and Lütkemeyer (1925) found that union of bromine atoms to form molecules occurred in only one collision out of every thousand at 200° C.; the result suggests that a three-body reaction is necessary, and if this were so the velocity constant should increase with the pressure. In the first experiments, which involved measurements of the rate of photochemical formation of hydrogen bromide from its elements, negative results were obtained and the three-body mechanism was discarded, but in a repetition of the work (Jost and Jung, 1929), with improved technique, the anticipated effect of pressure was observed. The influence of neutral gases on the reaction velocity is also in harmony with the three-body mechanism (p. 341).

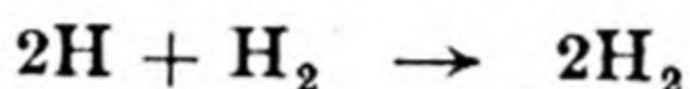
The long life of active nitrogen, which contains atoms of this element, is now generally attributed to the fact that union of the atoms can only occur when there is a collision of the type



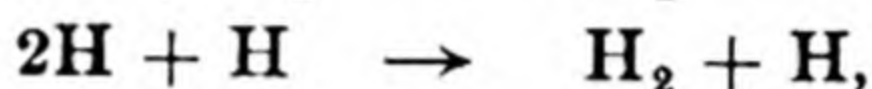


or else when two atoms meet at the walls of the vessel; the latter is capable of removing the excess energy of the resulting molecule. This ternary mechanism accounts for the fact that increase of pressure increases the velocity constant of the decay of active nitrogen (Kneser, 1928), and also for the negative temperature coefficient of the decay (Willey, 1928); as already indicated, the rate of a termolecular process may well decrease as the temperature is raised.

Smallwood (1929) and Amdur and Robinson (1933) have studied the rate of recombination of atomic hydrogen and found that the reaction is in general accord with the mechanism



or



the former process being more effective. Similar conclusions have been reached in connection with formation of deuterium molecules from atoms (Amdur, 1935). The combination of atoms also occurs at the walls of the reacting vessel to a small extent. The results indicate that as the pressure is increased the total rate of reaction increases, but the fraction of the combination occurring at the walls of the vessel decreases; in view of the increased number of impacts in the gas phase this observation is in agreement with the three-body collision mechanism.

## UNIMOLECULAR REACTIONS

**Decomposition of Nitrogen Pentoxide.** In 1924 the only reaction which was generally accepted as being definitely and unequivocally unimolecular and homogeneous was the decomposition of phosphine, investigated by Trautz and Bhandarkar (1919); in that year, however, Hinshelwood and Topley proved quite clearly that the reaction velocity was influenced by the surface of the reaction vessel and by the introduction of powdered material, and so the decomposition was heterogeneous. Daniels and Johnston (1921) had suggested that the thermal decomposition of nitrogen pentoxide vapour was a homogeneous reaction of the first order,



and although doubt was at first cast on this view, a great deal of subsequent investigation has proved quite conclusively that the process is unimolecular and homogeneous. In view of the importance of the nitrogen pentoxide decomposition in connection with the theory of unimolecular gas reactions the kinetics of the process has been studied under different conditions by a number of experimenters. It has been found, however, that the unimolecular velocity constant of the reaction at a given temperature is independent of the pressure, of the nature of the vessel, of the origin of the pentoxide, of the presence of inert gases, *e.g.*, hydrogen, carbon monoxide, bromine, chlorine, argon and nitrogen, and of various other factors (Hunt and Daniels, 1925). The values for the velocity constant at 65° C. obtained by Rice and Getz (1927) are of interest, and are quoted in Table LV.; for purposes of comparison it may be stated that Daniels and Johnston (1921) obtained a value of 0.292 at the same temperature.

TABLE LV.—*Velocity Constant for the Unimolecular Decomposition of Nitrogen Pentoxide at 65°*

Experimental Conditions.	<i>k</i> .
N <sub>2</sub> O <sub>5</sub> made from nitric acid and P <sub>2</sub> O <sub>5</sub> . . .	0.286
Gas filtered through blue asbestos . . .	0.284
Gas passed through electrical precipitator . . .	0.278
P <sub>2</sub> O <sub>5</sub> in reaction vessel . . . . .	0.278
N <sub>2</sub> O <sub>5</sub> made from silver nitrate and chlorine . . .	0.291

The results show that dust particles cannot be acting as catalysts, and also that the complete removal of moisture, which might presumably be present as nitric acid, does not influence the reaction. The decomposition of nitrogen pentoxide has been studied at various pressures, and the velocity constant is the same down to pressures of about 0.05 mm. of mercury; the reaction must be regarded definitely as unimolecular, even at very low concentrations. The velocity constant varies appreciably with temperature, and by substituting in the Arrhenius equation the



mean value of the energy of activation, between  $0^\circ$  and  $65^\circ$ , is found to be 24,700 cal. per gm. mol. of pentoxide. It is interesting to note that the decomposition of nitrogen pentoxide has also been found to be unimolecular in a number of inert solvents; in most cases the energy of activation is the same as that for the gaseous reaction (Eyring and Daniels, 1930).

**Unimolecular Processes.** Since 1926 a number of other homogeneous gaseous reactions of the first order have been brought to light, mainly as the result of the work of Hinshelwood and his collaborators in England, and of Ramsperger in the United States of America. Amongst these reactions are the decomposition of acetone vapour at about  $500^\circ$  C., of propionic aldehyde at  $450$ — $600^\circ$  C., of various ethers between  $400^\circ$  and  $600^\circ$  C., of azomethane, azo-isopropane and methyl-isopropyl di-imide at about  $300^\circ$  C., of ethyl bromide at  $300$ — $400^\circ$  C., and the isomerisation of gaseous

TABLE LVI.—*Homogeneous Unimolecular Gas Reactions*

Reaction.	Compound Decomposed.	No. of Atoms per Molecule.	<i>E</i> cal.	Minimum Pressure.	
				mm. Hg.	K.
Thermal decomposition of—					
Nitrous oxide .	$\text{N}_2\text{O}$	3	53,000	—	—
Nitrogen pentoxide .	$\text{N}_2\text{O}_5$	7	24,700	0.06	$308^\circ$
Acetone .	$\text{CH}_3\cdot\text{CO}\cdot\text{CH}_3$	10	68,500	—	—
Propionic aldehyde .	$\text{C}_2\text{H}_5\cdot\text{CHO}$	10	54,000	80	$700^\circ$
Dimethyl ether .	$\text{CH}_3\cdot\text{O}\cdot\text{CH}_3$	9	58,000	850	$700^\circ$
Diethyl ether .	$\text{C}_2\text{H}_5\cdot\text{O}\cdot\text{C}_2\text{H}_5$	15	58,000	150	$700^\circ$
Methyl ethyl ether .	$\text{CH}_3\cdot\text{O}\cdot\text{C}_2\text{H}_5$	12	54,500	190	$700^\circ$
Methyl propyl ether .	$\text{CH}_3\cdot\text{O}\cdot\text{C}_3\text{H}_7$	15	49,000	100	$700^\circ$
Di-isopropyl ether .	$\text{C}_3\text{H}_7\cdot\text{O}\cdot\text{C}_3\text{H}_7$	21	61,000	<29	$820^\circ$
Azomethane .	$\text{CH}_3\cdot\text{N}:\text{N}\cdot\text{CH}_3$	10	51,200	40	$560^\circ$
Azoisopropane .	$\text{C}_3\text{H}_7\cdot\text{N}:\text{N}\cdot\text{C}_3\text{H}_7$	22	40,900	<0.25	$560^\circ$
Methyl isopropyl di-imide .	$\text{CH}_3\cdot\text{N}:\text{N}\cdot\text{C}_3\text{H}_7$	16	47,480	80	$560^\circ$
Dimethyl triazine .	$\text{CH}_3\cdot\text{N}:\text{N}\cdot\text{NH}\cdot\text{CH}_3$	12	33,800	10	$500^\circ$
Ethylene oxide .	$\text{C}_2\text{H}_4\text{O}$	7	52,000	285	$617^\circ$
Propylamine .	$\text{C}_3\text{H}_7\cdot\text{NH}_2$	13	44,000	<200	$820^\circ$
Isopropylamine .	$\text{C}_3\text{H}_7\cdot\text{NH}_2$	13	42,600	<150	$820^\circ$
Dimethylamine .	$(\text{CH}_3)_2\cdot\text{NH}$	10	44,800	—	—
Ethyl bromide .	$\text{C}_2\text{H}_5\cdot\text{Br}$	8	54,000	100	$670^\circ$
Ethylidene diacetate .	$\text{CH}_3\cdot\text{CH}(\text{O}\cdot\text{CO}\cdot\text{CH}_3)_2$	20	—	—	—
Isomerisation of pinene	$\text{C}_{10}\text{H}_{16}$	26	43,710	—	—



pinene between  $184^{\circ}$  and  $237^{\circ}$  C. In the last case the unimolecular velocity constant is the same in the gas, in the pure liquid and in solution in various alcohols (D. F. Smith, 1927). Table LVI. contains some of the known reactions which are of the first order, together with the formulæ of the reactants and the number of atoms in the molecule of each. The heats of activation ( $E$ ) are also quoted, and the low pressure at which the reaction ceases to be kinetically unimolecular; the importance of these quantities will be seen shortly.

### MECHANISM OF UNIMOLECULAR REACTIONS

In a unimolecular reaction the period of half decomposition, and in fact the time taken to decompose any definite fraction of the original amount of reactant, is independent of the concentration (or pressure). In other words, for a given mass of gas the amount decomposed in unit time, *i.e.*, the rate of reaction, is independent of the pressure. The chemical change in such a reaction cannot, therefore, be a *direct* consequence of collision, since the fraction of the total number of gas molecules present in a given volume involved in collisions in unit time depends on the actual number of molecules in unit volume, and hence on the concentration (see p. 265). It may be seen from Table LVI. that the heats of activation, determined from the temperature coefficients, of unimolecular reactions are quite large, and so it may be assumed, in agreement with previous considerations, that the reacting molecules must acquire a fairly large amount of energy before they can decompose. The problem that now arises therefore is: how do these molecules acquire the necessary energy if interchange by collision is ruled out?

**The Radiation Theory.** The first definite views on the subject were expressed by Perrin in 1919; he considered that since the amount of reactant decomposed in a given time is independent of the pressure it should be possible to expand a definite mass of gas to infinite volume without altering the number of molecules undergoing change in unit time. If this argument is correct, then isolated molecules, prevented from acquiring energy by collision,



should have the capacity of becoming activated and decomposing. The only source of energy which appeared to Perrin to be available was radiation, and it was considered that in a unimolecular reaction molecules became activated as a result of the absorption of radiation of the appropriate frequency. This theory appeared to fit in well with the wider radiation theory of chemical action originally proposed in a vague form by Trautz (1906) and subsequently elaborated by W. C. McC. Lewis in a number of papers from 1916 onwards.\* It may be stated at the outset that the general radiation theory is now purely of historical interest, as in spite of its great attractiveness it did not survive the stringent experimental tests to which it was subjected. The idea of radiation as the source of energy in unimolecular reactions, however, requires some further consideration.

The heat of activation ( $E$ ) of nitrogen pentoxide is 24,700 cal., and so this quantity of energy must be absorbed before a gm. mol. of the compound can decompose; if this is taken up as a quantum of radiant energy, then according to the Planck theory the frequency  $\nu$  of the activating radiation is given by

$$Nh\nu = E \quad \dots \dots \dots (ix.)$$

where  $N$  is the Avogadro number, and  $h$  the Planck constant, expressed in the same energy units as  $E$ . The value of  $h$  is known to be  $6.547 \times 10^{-27}$  erg-second, and this is equivalent to  $6.547 \times 10^{-27}/4.185 \times 10^7$  cal. per sec.; hence

$$\frac{6.06 \times 10^{23} \times 6.547 \times 10^{-27}}{4.185 \times 10^7} \times \nu = 24,700$$

$$\therefore \nu = 2.6 \times 10^{14} \text{ vibrations per sec.}$$

The wavelength of the radiation possessing this frequency is  $1.15\mu$ , and this particular radiation should be effective in activating nitrogen pentoxide and accelerating its decomposition. In other words, the influence of this radiation should be the same as that of raising the temperature in increasing the proportion of activated molecules, and so increasing the reaction velocity. Various investigators have subjected nitrogen pentoxide to light of wavelength  $1.15\mu$ , but no acceleration in the rate of decomposition was



observed, even at low pressures when, as will be shown subsequently, the effect might have been more marked (Kassel, 1929). It may be argued that the energy of activation is not absorbed in a single quantum direct from the normal state of the molecule; if this were so the effective radiation would not necessarily have a wavelength of  $1.15\mu$ . Observation has shown that nitrogen pentoxide is only decomposed by radiations in the blue region of the spectrum, and then only in the presence of nitrogen dioxide as a photocatalyst. The same failure of the theoretically active radiations to influence the reaction velocity has been found with other unimolecular reactions. It must be concluded, therefore, that the radiation theory is not adequate to account for the activation of molecules in homogeneous reactions of the first order.

Other theories of the mechanism of unimolecular changes have been proposed, but two only, which seem to be the most reasonable, will be discussed here, although not in chronological order. Both these suggestions involve the idea that the origin of the activation, in spite of what has already been said, is due to collision between molecules; it remains to be explained, therefore, why the fraction of the total number of molecules decomposed in unit time is independent of the pressure.

**The Chain Theory.** Christiansen and Kramers (1923) consider that the products of the reaction, which possess energy equal to the heat of reaction as well as to the original heat of activation, are able by collision to transfer this energy to molecules of reactant and so activate them. That is to say, the first reacting molecule sets up a "reaction chain." Each activated molecule as it decomposes and is removed from the system is thus able to cause the activation of another molecule. The fraction of the total number of molecules possessing the activation energy is, in the first place, determined by the Maxwell distribution, and, according to the reaction chain theory, if any one of these is decomposed it is replaced by another. Some of the active molecules will, of course, be de-activated by collisions and the number of activated molecules at any instant will remain a definite fraction of the total number. The rate of reaction at a given temperature will consequently be directly proportional to the number of molecules of the



reactant only, and independent of the pressure ; this is, of course, the criterion of a unimolecular reaction.

If an inert gas is added to the reacting system there are increasing chances that the molecules of the reaction product carrying their excess energy will be de-activated by collision with these inert molecules instead of with molecules of reactant ; if this were the case the presence of an inert gas would destroy the unimolecular nature of the reaction, which would then tend to become one of the second order. The same tendency to change from a unimolecular to a bimolecular mechanism should also occur as the inactive reaction products accumulate, and deprive the newly formed molecules of their excess energy. Actually no such influence of inert gases or of reaction products is observed, and so the chain reaction theory meets with a serious objection. In order to overcome this difficulty Christiansen and Kramers assume that the reaction products can only be deprived of their excess energy by collision with molecules of the reactant ; this assumption is not, of course, an impossible one, but on general grounds it does not seem altogether probable.

The reaction chain theory has also to contend with another difficulty : Tolman (1925) has shown that the homogeneous decomposition of nitrogen pentoxide is almost certainly an *endothermic* process. The actual heat of reaction is not known definitely, as the exact nature of the primary stage of the decomposition is uncertain, but in each of the possible mechanisms heat is absorbed. It follows, therefore, that the reaction products, oxides of nitrogen and oxygen, between them possess *less* energy than that required to activate a single molecule of nitrogen pentoxide. This objection to the theory, at least as far as the reaction under discussion is concerned, does not seem easy to overcome.

**The Collision Theory.** An alternative mechanism for unimolecular decomposition, the main idea of which was suggested in the first place by Lindemann (1922), has attracted much attention in recent years. It is supposed that the reacting molecules acquire their energy of activation as a result of impact with others, but that they only decompose when a certain period of time has elapsed after this impact. If the average time interval



between activation and decomposition is large compared with that between two impacts, the majority of the activated molecules will lose some of their energy by another collision before they have time to react. In general, therefore, only a small fraction of the active molecules present at any instant will succeed in decomposing. The rate of activation by collision, which does depend on the gas pressure, is thus quite different from the rate of reaction.\* Since most of the active molecules soon become de-activated by collisions with molecules of low energy content, the proportion decomposing is not large enough to affect the ordinary Maxwell distribution of energy amongst the molecules of the gas as a whole. The number of active molecules, possessing the appropriate amount of energy for reaction, will thus be a definite fraction of the total number. Since the number decomposing in a given time is a definite fraction of the active molecules, it follows that the fraction of the molecules decomposed is directly proportional to the total number of molecules of reactant present, irrespective of the volume they occupy (or their pressure); this is the condition which a unimolecular process must satisfy. The Lindemann mechanism, although it involves activation by collision, can thus account for the fraction decomposed being independent of pressure.

**The Effect of Pressure Reduction.** As the pressure of a gas is decreased the average time between two successive collisions undergone by a particular molecule becomes greater; eventually a pressure is reached at which this interval is equal to the time elapsing between the activation of a molecule and its decomposition. At this pressure, and at all lower values, every molecule which acquires the energy of activation in a collision will decompose before it can be de-activated. The rate of reaction is then equal to the rate of formation of activated molecules as a result of collisions; the process, therefore, should appear to be kinetically bimolecular at low pressures. The following simple mathematical treatment will make the point clear. The rate of activation of molecules is proportional to the number of collisions and con-

\* In reading this section it is important to remember that the rate of activation of molecules, and the number of active molecules present at any instant, are quite distinct; the former depends on the number of collisions, and the latter on the Maxwell distribution.



sequently to the square of the concentration of normal molecules, which is practically the same as the total concentration ; that is

$$\text{rate of activation} = k_1 c^2.$$

The rate of de-activation of active molecules by loss of energy to normal molecules in collisions is proportional to the concentration of active molecules ( $a$ ) and of normal molecules ( $c$ ); hence

rate of de-activation =  $k_2ac$ .

The activated molecules undergo transformation, when they are not de-activated, at a rate which may be represented by  $k_3a$ , and so for a stationary concentration of active molecules :

$$k_1 c^2 = k_2 ac + k_3 a \quad . \quad . \quad . \quad . \quad . \quad . \quad (x.)$$

$$\therefore \text{Rate of reaction} = k_3 a = k_1 c^2 / (k_2 c / k_3 + 1) \quad \text{. . . (xi.)}$$

If  $c$  is large, then  $k_2 c / k_3$  is large in comparison with unity and the latter may be neglected in the denominator of equation (xi.), and so

$$\text{rate of reaction} = c(k_1k_3/k_2); \quad \dots \quad (\text{xii.})$$

the reaction is thus unimolecular, the rate being proportional to the concentration of reacting molecules. When  $c$  becomes small, however, that is at low pressures,  $k_2c/k_3$  may be neglected and the rate of reaction becomes proportional to  $c^2$ ; the process then appears to be kinetically bimolecular.

As long as the pressure is high the reaction is unimolecular and the time to complete a given fraction of the reaction, say 50 per cent., will be independent of the initial pressure. At low pressures, however, the reaction tends towards the second order and the time for half-decomposition will be inversely proportional to the initial pressure; it should, therefore, increase as the initial pressure is decreased. This effect to be anticipated from the Lindemann theory of unimolecular reactions has been definitely observed in the decomposition of a number of ethers, and of propionic aldehyde and other compounds; at ordinary pressures the reactions are undoubtedly unimolecular, but at low pressures the rates decrease. In the following Table LVII. are given the times in seconds ( $t_{50}$ ) for the pressure to increase by 50 per cent. of



the initial value in the homogeneous decomposition of methyl propyl ether at 425° C.

TABLE LVII.—*Rates of Decomposition of Methyl Propyl Ether at 425° C.*

Pressure (mm.).	336	281.5	228	195.5	181	142.5
$t_{50}$ (secs.)	216	210	207	216	201	213
Pressure (mm.).	137	118	111	77	46.5	22
$t_{50}$ (secs.)	216	219	230	270	345	393

Although  $t_{50}$  does not represent the time for half-decomposition, it does correspond to the decomposition of a definite fraction of the amount of methyl propyl ether present originally. The time to complete this fraction is clearly independent of the pressure, as required for a unimolecular reaction, down to a pressure of about 110 mm. of mercury; below this value the rate of decomposition falls off, as shown by the increase of  $t_{50}$ . Similar behaviour has been observed with other ethers and in the decomposition of various aliphatic compounds; the reactions are all unimolecular at high pressures, but not so at low values. The actual pressure at which the decrease occurs varies somewhat with the temperature, and the approximate limiting pressures, at the temperatures quoted, are given in Table LVI.

These results form one of the most convincing pieces of evidence in favour of the idea that activation, even in a unimolecular reaction, occurs by collision. For several years it was considered that the decomposition of nitrogen pentoxide remained unimolecular down to pressures of 0.002 mm. of mercury (Hibben, 1927); in 1930, however, Schumacher and Sprenger, and Ramsperger and Tolman, independently, found that at pressures of about 0.05 mm. at 85° C. the reaction rate showed the expected decrease. By working with a vessel of 45 litres capacity the latter authors proved that previous work had been in error because of the influence of the walls of the reaction vessel. At a pressure of 0.001 mm. the observed order of the reaction is 1.8 (Linhorst and Hodges, 1934).



**Influence of Hydrogen Molecules.** A very interesting observation has been made by Hinshelwood: he found that in the presence of hydrogen the decrease in reaction velocity at low pressures, during the decomposition of ethers and of propionic aldehyde, did not occur. The products of the reaction appear in some cases to have the same effect, but other inert gases, *e.g.*, helium and nitrogen, are unable to prevent the falling off in the rate of reaction. It is clear that the hydrogen is not entering into any chemical action, since it does not increase the reaction velocity at high pressures; its effect is simply to extend the pressure range over which the process is kinetically unimolecular. The function of the hydrogen is apparently to maintain the Maxwell distribution at low pressures; in other words, the molecules of hydrogen behave just like molecules of reactant in being able to de-activate the active molecules before they can decompose, and to activate others by collision. It therefore maintains the rate of activation, which would otherwise have fallen off. The presence of hydrogen ensures that the number of active molecules at any instant remains a definite fraction of the total number, at pressures much lower than would have been possible in its absence. The unimolecular reaction rate is thus kept constant at very low pressures. The behaviour of hydrogen in this connection has been attributed to (a) the high speed of the molecules, which means a high collision frequency, and (b) the fact that each molecule has five degrees of freedom, and so possesses a large amount of energy— $RT/2$  per degree of freedom—available for transfer. Helium molecules also move rapidly, but having only three degrees of freedom are not so effective in maintaining the Maxwell distribution of energy amongst the other molecules.

**Influence of Reaction Products.** In the decomposition of methyl propyl ether it appears that ethane, one of the reaction products, is effective in maintaining the unimolecular rate; although this substance has not a very high molecular velocity, it has, with its eight atoms, a large number of degrees of freedom, and so is likely to be effective in producing the energy interchange necessary for the maintenance of the Maxwell distribution. It must not be considered, however, that apart from a high velocity



a large number of degrees of freedom is sufficient for a molecule to be effective in this respect ; there is little doubt that the ability of one type of molecule to act as a means of energy interchange between others is a specific property. It is possible that the reaction products may be responsible for the fact that the decomposition of nitrogen pentoxide remains unimolecular down to such low pressures.

**Number of Molecular Collisions.** If it is considered that in a unimolecular process activation occurs as a result of collisions it must follow that the number of such collisions involving activated molecules should be at least equal to the rate of decomposition. For the decomposition of acetone Hinshelwood and Hutchison (1926) found the energy of activation, from the temperature coefficient of the velocity constant, to be 68,500 cal. per gm. mol. ; if  $\sigma$ , the effective diameter, is taken as  $5 \times 10^{-8}$  cm., and the root mean square velocity,  $\bar{u}$ , is  $6 \times 10^4$  cm. per sec. at  $835^\circ$  K., then at this temperature and a pressure of 760 mm. of mercury ( $n = 8.85 \times 10^{18}$  molecules per c.c.), the maximum number of molecules activated by collision in 1 c.c. per second

$$= \sqrt{2\pi\sigma^2\bar{u}n^2} \times e^{-E/RT}$$

$$= 0.54 \times 10^{11}.$$

Experiments have shown, however, that at  $835^\circ$  K., and a pressure of 1 atm.  $1.33 \times 10^{16}$  molecules of acetone are actually decomposed every second in one cubic centimetre ; this is nearly a million times as great as the apparent maximum rate of activation by collision.

**Origin of Energy of Activation.** At first sight it would appear that the collision mechanism fails completely and that a chain mechanism must be assumed to account for the actual rate of the reaction, but it must be remembered that the use of the term  $e^{-E/RT}$ , to represent the fraction of the colliding molecules which become activated, is based on the assumption that the energy available is expressed in *two* square terms only, that is, in two degrees of freedom. It has been suggested, therefore, that when a molecule undergoes unimolecular decomposition the energy of activation does not come merely from the translational energy, or



other form expressible in two square terms only, but the energy in several internal degrees of freedom—rotational and vibrational—can contribute towards the energy of activation. The quantity  $E$  can, therefore, be made up in a number of different ways, and the number of molecules capable of becoming activated is thus much greater than if the energy is restricted to two degrees of freedom only. This idea has been developed by Hinshelwood and by Fowler and Rideal (1926), and the former has shown that for a molecule with energy expressible in  $s$  square terms which is able to count towards the activation energy, the fraction of the total number of molecules with energy greater than  $E$  is given by the expression

$$\frac{e^{-E/RT} (E/RT)^{\frac{1}{2}s-1}}{\frac{1}{2}s - 1}$$

If  $s$  is large, *e.g.*, of the order of 10 to 20, this factor is found to be very much larger than  $e^{-E/RT}$ , and is capable of accounting for the apparent discrepancy between the rate of activation and that of decomposition. Utilising the new factor for the probability that a particular molecule will be activated, and using the method previously developed (p. 265), it is found that

$$\frac{d \ln k}{dT} = \frac{E - (\frac{1}{2}s - 1)RT}{RT^2} \quad \dots \quad \text{(xiii.)}$$

The true energy of activation ( $E$ ) is thus greater than the value obtained from the Arrhenius equation by an amount  $(\frac{1}{2}s - 1)RT$ ; this difference only becomes appreciable at high temperatures if  $s$  is large. The temperature coefficient of the reaction is therefore of the same type as when the simple exponential factor,  $e^{-E/RT}$ , is involved.

**Number of Degrees of Freedom.** As long as a reaction is kinetically unimolecular the rate of activation is by the Lindemann theory much greater than the rate of decomposition; when the velocity constant *just* begins to fall off as the pressure is diminished it may be assumed that the rate of reaction is then of the same magnitude as the rate of activation. By equating the number of molecules reacting in one cubic centimetre per second at this



limiting pressure with the rate of activation in the same volume an approximate value of  $s$  may be calculated. Working in this manner Hinshelwood has determined the values given in Table LVIII.

TABLE LVIII.—*Number of Square Terms ( $s$ ) Involved in Energy of Activation*

Decomposition of :					$s$
Nitrous oxide	.	.	.	.	2
Diethyl ether	.	.	.	.	8
Methyl ethyl ether	.	.	.	.	9
Dimethyl ether	.	.	.	.	11
Propionic aldehyde	.	.	.	.	12
Methyl propyl ether	.	.	.	.	12
Azomethane	.	.	.	.	25
Nitrogen pentoxide	.	.	.	.	30
Methyl isopropyl di-imide	.	.	.	.	33
Azoisopropane	.	.	.	.	> 40

Since each internal degree of freedom in the molecule involves two square terms, the values of  $s$  do not appear to be impossibly large.

The most striking, and probably very significant, fact concerning unimolecular reactions is that most of the substances involved are of complex internal structure (see, however, p. 301). It is with such substances, involving many different vibrations, that a time lag between activation and decomposition might be expected, and it is this delay which is responsible for the rate of reaction being independent of the pressure. On the other hand, the high rate of activation necessary to account for the observed velocities of unimolecular decompositions requires that energy from a fairly large number of different degrees of freedom should be available for activation purposes; it is only with such molecules of complex internal structure that this number is available. The mechanism proposed by Lindemann, and its extension by Hinshelwood, and others, thus seems a very plausible move in the direction of clarifying the problem of unimolecular reactions.

Although it has been assumed here that the value of  $s$  remains



constant, Steacie and Solomon (1934) account for the influence of pressure on the decomposition of ethyl ether by postulating that  $s$  is proportional to the time between molecular collisions. According to this suggestion, which is fundamentally not unreasonable, the number of square terms contributing to the energy of activation should decrease as the pressure increases. Steacie is of the opinion that this would account for the effect of pressure on the velocity constant for the decomposition of acetaldehyde, and presumably of other substances, in connection with which Fletcher and Hinshelwood (1933, 1934) suggested that several different types of activation were possible.

**Activation of Particular Degrees of Freedom.** A modification of the general theory has been suggested by Rice and Ramsperger (1927), and by Kassel (1928); these authors agree in thinking that the time interval between activation and decomposition decreases proportionately as the energy content of the active molecule exceeds the minimum amount required for activation. According to the simple theory already discussed this interval is assumed to be independent of the energy, provided the latter is in excess of the critical amount. In addition Rice and Ramsperger consider that a particular degree of freedom, rather than the molecule as a whole, must acquire the energy of activation before the molecule can decompose; Kassel, on the other hand, is of the opinion that a particular valency bond, involving two degrees of freedom, must acquire the activation energy. The greater the total energy of the molecules, acquired as the result of a collision, the more rapidly will the necessary energy "flow" into the degree of freedom, or valency bond, and so the shorter the time lag between activation and decomposition. On the basis of these views both Rice and Ramsperger, and Kassel, deduced complicated formulæ connecting the velocity constant of the reaction with the pressure of the gas; a much simpler relationship, similar to equation (xi.), can be deduced from the original theory, but it is claimed that the results obtained in the decomposition of azomethane are in better agreement with the newer formulæ. According to the original Hinshelwood-Lindemann theory of activation of the molecule, the curve of  $k_{\infty}/k$  against  $p$ , where  $k_{\infty}$  is the unimolecular velocity



constant at high pressures and  $k$  the observed constant at a pressure  $p$ , should be almost independent of temperature; the modified theory, however, requires that the velocity coefficient ( $k$ ) should begin to fall off at a higher pressure the higher the temperature. It is true that an effect of this type has been observed in the decomposition of azomethane and of methyl propyl ether, although not of methyl ethyl ether, but as Hinshelwood (1929) points out "it is unsafe to draw from these results theoretical conclusions about the activation process itself, since the influence of the reaction products, and other secondary effects, must distort the picture to some extent." Vernon and Daniels (1933) have recently made a complete study of the unimolecular decomposition of ethyl bromide and conclude that their results favour the Rice-Ramsperger-Kassel point of view. The observations with nitrogen pentoxide do not appear to be in harmony with either theory (Linhorst and Hodges, 1934).

**Unimolecular and Bimolecular Reactions.** The theories discussed in this chapter imply that there is no fundamental difference between the unimolecular and the bimolecular decomposition of a single reactant. For this reason the former are often called "quasi-unimolecular" processes. If the time lag between activation and reaction is small in comparison with the interval between two successive collisions, then the rate of reaction is proportional to the number of collisions, and hence the process is bimolecular. This occurs with substances of simple constitution. When the time lag is large, however, as it is for complex molecules, the reaction is kinetically unimolecular. From equation (x.) it may be seen that if  $k_3$  is large, that is, the activated molecules have a high rate of decomposition, corresponding to a small time interval between activation and reaction, the term  $k_2c/k_3$  will always be small and may be neglected. The resulting relationship is then that for a bimolecular reaction, whereas if  $k_3$  is small and the time lag appreciable the reaction is kinetically of the first order. The absence of any fundamental distinction between molecules undergoing unimolecular and bimolecular reactions is brought out by the discovery, due to Volmer (1930), that the thermal decomposition of nitrous oxide is



definitely homogeneous and unimolecular at pressures of the order of a few atmospheres. Hinshelwood and Burk (1924) had previously considered this reaction to be bimolecular, but later Hinshelwood (1932) came to the conclusion that uni- and bimolecular reactions were occurring simultaneously at ordinary pressures. As a result of a study of the decomposition of nitrous oxide at pressures up to 40 atm., Hunter (1934) considers that three quasi-unimolecular reactions are occurring simultaneously. The pressures above which they are kinetically of the first order are 0.08, 5 and 30 atm., respectively; hence above 30 atm. the decomposition appears to be exclusively unimolecular, whereas below 0.08 atm. it is entirely bimolecular.

Two points of difference, which may be of importance in the theory of gas reactions, between simple and complex molecules are worth noting. The first point is that if activation of a particular bond or degree of freedom were required before a molecule could decompose, it is natural that this condition should be attained more readily with a simple molecule where only very few degrees of freedom are possible; with a complex molecule, however, a considerable time might elapse between collision and the acquisition by the critical bond of its requisite energy. Secondly, Kornfeld (1927) has indicated that if simple compounds were to decompose in a unimolecular manner free atoms would result and the necessary energy of activation, on account of the large negative heat of reaction, would probably be very great. Such decompositions do not, therefore, occur. Complex molecules can readily disintegrate into simpler molecules; accordingly the energy of activation is low, and unimolecular reactions are possible. This is, of course, not the whole story, but it is a factor worth keeping in mind.

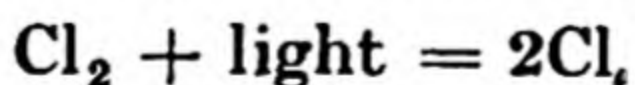
## CHAIN REACTIONS

**The Energy Chain Theory.** The idea that the products of a particular act of chemical transformation may initiate further acts and so lead to a reaction chain appears to have been first suggested by Bodenstein (1913); it was proposed in order to account for the

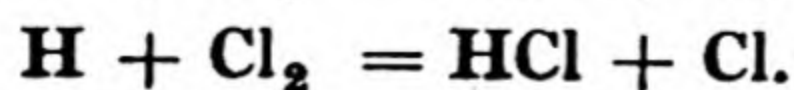
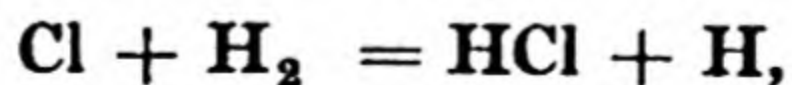


abnormally high yields of hydrogen chloride, for a given light intensity, obtained in the photochemical union of hydrogen and chlorine (see Chapter VI.). The mechanism suggested originally involved the presence of "wandering electrons," but it was subsequently modified (1916) into the following theory: it is supposed that the molecules of the reaction product (hydrogen chloride) at the instant of formation bear the heat of reaction, together with any energy of activation of the reactants, which they are able to transfer by collision to, and so activate, molecules of reactant, *e.g.*, chlorine. In this way every primary act of combination or decomposition, brought about by suitable means, sets off a reaction chain resulting in the combination or decomposition of many thousands of molecules. These reaction chains might be broken as a result of de-activating collisions with neutral molecules, or by collisions with the walls of the containing vessel; such impacts are generally termed "non-elastic" collisions. The concept of a chain reaction, as already mentioned, was used by Christiansen and Kramers to account for unimolecular reactions, although it was assumed that de-activation of the product could only occur as a result of collisions with molecules of the reactant. It is true that the formation of reaction chains is not necessarily the cause of first order processes, but similar chains undoubtedly occur in other cases. The theory of chain reactions described here is called the "hot molecule" or "energy chain" theory, because of the high energy content of the molecules of the product; it will be shown later that this chain mechanism is probably operative in many reactions.

**The Material Chain Theory.** An alternative type of chain mechanism, called the "atom chain" or "material chain" theory, was proposed by Nernst (1918) to account for the high yields in the hydrogen-chlorine reaction. He suggested that the primary effect of light was to decompose the chlorine into atoms, thus

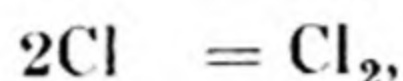


and then the series of reactions followed:





The atom of chlorine, after causing a molecule of hydrogen and one of chlorine to combine, is evidently regenerated and able to cause further reaction ; each chlorine atom is thus the source of a reaction chain. These chains could be terminated in one, or more, of the following ways :



and



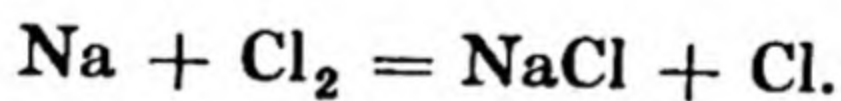
In many reactions it is important to decide which type of chain mechanism is operative, but it is probable that both can occur. Many reactions are more readily explicable on the basis of one kind of chain, whereas others seem to be more in harmony with the other ; in some circumstances both types can occur. With photochemical processes the band spectrum of the reacting molecules often provides a means of determining which of the two methods of carrying on the reaction chain is the more probable (see Chapter VI.).

**Evidence for Chain Reactions.** There is good reason, apart from the high photochemical yield, to believe that reaction chains do occur in the hydrogen-chlorine reaction ; if this is proved, the idea of chains may be extended to other processes. Weigert and Kellermann (1923) observed that when a mixture of hydrogen and chlorine was exposed momentarily to light the resulting chemical change, as indicated by alteration in the index of refraction of the mixed gases brought about by the heat of reaction, did not develop to its full extent until a definite fraction of a second after the light had been cut off. This result indicates that the light sets up a chain of reactions which continues for an appreciable time even in the dark. Another important piece of evidence is due to Lind and his co-workers (1926, 1930) ; these authors found that the extent of combination of hydrogen and chlorine, and of carbon monoxide and chlorine brought about by light and by the action of  $\alpha$ -particles is almost the same (see p. 323). In each case the reaction products are in excess of the amounts anticipated from the intensity of the stimulating agent. The primary act of chemical union is caused by quite different means in the two

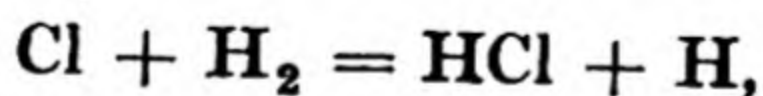


processes, but each act, whatever its origin, is apparently capable of initiating the same reaction chain. Both the light and the  $\alpha$ -particle can thus act as "triggers" in setting off exactly the same series of chemical changes; it would be difficult to account for this behaviour without assuming the existence of a chain reaction. Similar observations have been made by Bäckström and Alyea (1928) during the oxidation of sulphite solutions in the presence of various alcohols as inhibitors; the reaction may be induced thermally or photochemically, but the chain length is the same in each case (see also Chapter VI.).

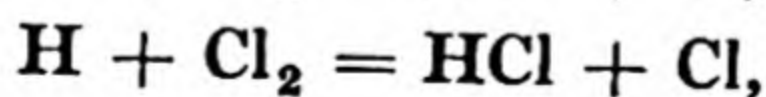
Nernst chains probably arise only when a reaction is induced in an appropriate manner: either by means of suitable radiation, or by a chemical change vigorous enough to yield atoms. A probable example of the former type of stimulus has been mentioned in the photochemical union of hydrogen and chlorine (see also p. 341); an example of the latter type has been studied by Polanyi (1927). Hydrogen at a pressure of 5—15 mm., saturated with sodium vapour, by passage over the heated metal, is mixed with chlorine at 0.2—0.3 mm. pressure; sodium chloride is formed, but so also is hydrogen chloride in much larger amounts. The production of the latter cannot be due to normal chemical action, as it takes place at a lower temperature than that at which ordinary combination is appreciable; the most reasonable explanation is that the sodium-chlorine reaction produces an atom of chlorine (p. 272), thus



This atom then initiates a Nernst atom-chain involving hydrogen, as follows:



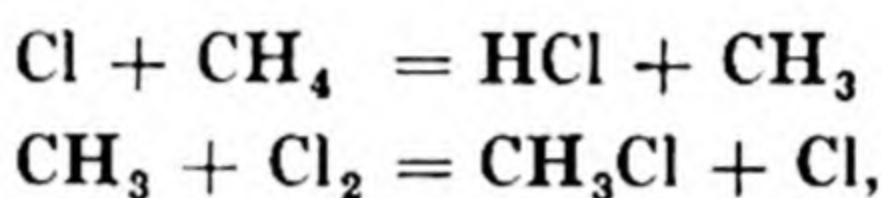
and



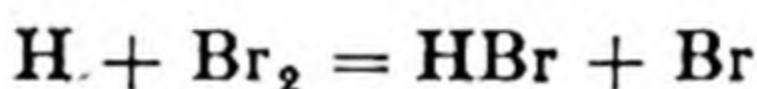
and so on; each act of combination between sodium and chlorine will thus result in the formation of many molecules of hydrogen chloride. The chain may not only be terminated by the union of two hydrogen, or of two chlorine, atoms, but it appears that the walls of the vessel are also effective in breaking the chains. If nitrogen is added the chain lengths, as evidenced by the ratio of



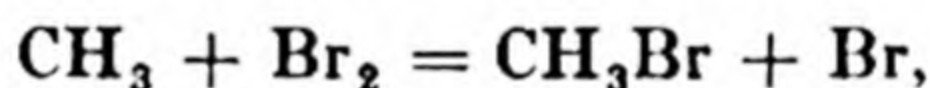
hydrogen chloride to sodium chloride produced, are increased; the molecules of the inert gas operate simply by reducing the chances of access of the atoms to the walls, where they become de-activated in some manner. Increase of the hydrogen pressure also increases the chain length for the same reason. The length of the chains may be increased tenfold if the walls of the reaction vessel are covered with a compact layer of sodium chloride; this substance does not tend to react with chlorine or hydrogen atoms, and so does not have any marked effect in terminating the reaction chains. Polanyi has observed a similar chain reaction when using methane, or other hydrocarbon, in place of hydrogen; as before, a chlorine atom from the sodium-chlorine reaction initiates the chain



and so on. In both the reactions mentioned the addition of bromine produces a decrease in the chain length; according to Polanyi this occurs because the bromine combines with hydrogen atoms or with the methyl radical, thus



or



and the bromine atom is presumably not able to carry on the chain in the same manner as is the chlorine atom. The chains are thus more liable to be terminated in the presence of bromine.

**Chain Reaction Phenomena.** The evidence for chain mechanisms in the reactions discussed is mainly of a direct nature, but there are many other processes which occur so rapidly that it is impossible to account for the velocities on the basis of the simple theory of reaction by kinetically activated molecules. In these instances only a chain mechanism will account readily for the explosive violence with which the reactions occur; examples are the oxidation of ethylene, acetylene, methane, hydrogen, phosphine, carbon monoxide, sulphuretted hydrogen and methyl alcohol and benzene vapours, the reaction between hydrogen bromide and ozone, and the thermal decomposition of ozone sensitised by bromine vapour. Further, certain phenomena



have been observed in these reactions which do not seem to be explicable by any other than a chain mechanism. For example, at above  $520^{\circ}\text{C}$ . hydrogen and oxygen undergo homogeneous combination: the reaction is retarded by the walls of the vessel and markedly accelerated by steam, argon, nitrogen and helium, with relative efficiencies 5 : 4 : 3 : 1. The retarding action of the walls is accounted for by the supposition that reaction chains are broken there, and neutral gases accelerate the reaction by decreasing the possibility of access of active molecules to the walls of the vessel; it is significant that the order of effectiveness of these gases is in the inverse order of their diffusion coefficients (Gibson and Hinshelwood, 1928). The remarkable phenomena of upper and lower critical explosion limits, discussed later (p. 309), provides strong indirect evidence for the propagation of reaction chains in various reactions.

**Unimolecular Reactions and Chain Processes.** It has been shown by Rice and Herzfeld (1934) that it is possible, theoretically, for a chain reaction involving free radicals to be apparently kinetically of the first order. It is of considerable interest to enquire whether any of the reactions which have been generally accepted as unimolecular and homogeneous are really chain-processes. The rate of decomposition of propylamine (Sickman and Rice, 1935) and of methylamine (Emeléus and Jolley) are both diminished by an increase in the surface of the reaction vessel: this definitely suggests a chain mechanism, although the reactions are apparently of the first order. The introduction of free radicals into methyl ether induces decomposition of the latter by a chain process (Leermakers, 1934), but this does not prove that the normal thermal decomposition involves free radicals or a chain mechanism. The decompositions of ethyl ether (Steacie, 1936) and of diethyl hydrazine (Taylor and Ditman, 1936) are said to involve chains: both these processes are, in any case, very complex. Recent work by Staveley and Hinshelwood (1936) indicates that free radical reaction chains occur to some extent in the unimolecular decomposition of propaldehyde and of ether: the chains are, however, probably short and account for part only of the reaction. The whole problem is likely to be the



subject of further investigation (see "Recent Advances in General Chemistry," Chapter IX.).

### KINETICS OF CHAIN REACTIONS

It has been already seen that in a reacting system consisting of a single gas a kinetically unimolecular reaction would be possible as a result of a particular type of chain mechanism; it must be assumed, however, that the "hot" molecule can only have its energy removed by collision with a molecule of reactant, and by no other means (p. 292). This condition is probably rarely operative, and de-activation can occur as a result of impacts with other molecules and also at the walls of the reaction vessel. The relative extent of these two types of de-activation depends on the nature of the chain reaction and on the experimental conditions; for example, in the oxidation of methyl alcohol vapour most of the chains are terminated at the walls of the vessel, but when benzene vapour is oxidised the majority of the chains appear to be broken in the gas (Fort and Hinshelwood, 1930). In some of the reactions discussed below it will be seen that at low pressures chains are terminated mainly at the walls, but at high pressures most of the chains appear to be broken in the gas phase.

**Stationary Chains.** In general, for a chain reaction involving one or more gases it can be shown that

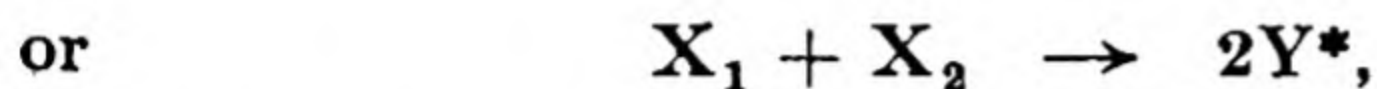
$$\text{Rate of reaction} = \frac{F(c)}{f_s + f_c + A(1 - a)} \quad \text{. . . (xiv.)}$$

where  $F(c)$  is a function of the concentration of the reacting gases;  $f_s$  and  $f_c$  represent the factors for the breaking of chains by the surface and by collisions with inert molecules, respectively;  $A$  is generally a constant, which is many times greater than  $f_s$  and  $f_c$ , and  $a$  is the average number of active molecules of product, capable of initiating chains, formed from each active molecule of reactant. As a general rule  $a$  will be equal to unity: that is, each reacting molecule yields one active molecule of product which starts off a chain. The reaction velocity under these conditions ( $a = 1$ ) will then be quite definite, and dependent on the length



of the chains ; this length is determined by the values of  $f_i$  and  $f_c$ . A chain reaction of this type is called a "stationary chain." If  $a$  is less than unity, and not all the reacting molecules succeed in initiating chains, the reaction velocity is quite small because  $A$  is so large, possibly  $10^5$  times as great as the sum of  $f_i$  and  $\bar{f}_c$ .

**Non-Stationary Chains.** On the other hand, if  $a$  is greater than unity, as might occur in highly exothermic reactions of the type



where each molecule of  $Y^*$  has enough energy to start a chain, the consequences are very interesting. In these circumstances  $1 - a$  is negative, and  $a$  does not need to be very large for  $A(1 - a)$  to become equal and opposite in sign to  $f_c + f_i$ ; the reaction velocity, according to equation (xiv.), is then infinite ! Since each reacting molecule is replaced by more than one activated molecule it is clear that a number of branching chains are set up, so that the reaction velocity increases from the commencement until it reaches such a high value that an explosion occurs. This is known as a "non-stationary" chain. It must be mentioned that the mechanism of this type of explosion is really different from that involved in a thermal explosion when the reaction velocity reaches a very high value simply as the result of a temperature increase, and the consequent increase in the number of molecules acquiring the energy of activation as a result of normal collisions ; in other words in a thermal explosion the high reaction velocity is due to the  $e^{-E/RT}$  function being large. No chain mechanism is implied in such cases, although *stationary* chains, which are not directly responsible for the explosion, may exist.

## CRITICAL PRESSURE LIMITS

**Pressure Limits of Explosions.** The relative magnitudes of  $f_c$ ,  $f_i$  and  $A$  can apparently alter with the pressures of the reacting gases and as a result of the presence of foreign gases. It is possible,

\* The asterisk indicates that the molecule carries a large excess of energy, which may be transferred to, and so activate, a molecule of reactant.



therefore, to find as the pressure is altered that at one point  $f_s + f_c + A(1 - a)$  is positive and the reaction velocity is definite and measurable, but at a slightly larger pressure the quantity  $f_s + f_c + A(1 - a)$  becomes equal to zero, and the speed of the reaction increases rapidly from the commencement and becomes explosive. This led to the remarkable phenomenon, studied originally by Semenov (1927) and by Hinshelwood (1928), of a reaction being comparatively slow at certain pressures, but either above or below a certain critical value the reaction suddenly becomes very rapid. Below a certain pressure the reaction between phosphorus vapour and oxygen, at ordinary temperatures, is negligibly small, but above this value it becomes extremely vigorous and even explosive, with marked chemiluminescence (Chariton and Walta, 1926; Semenov, 1927). Above another critical pressure of oxygen this luminescence, that is the "glow of phosphorus," as is well known, ceases once again.

**Breaking Reaction Chains.** Semenov has suggested that a branched chain mechanism is operative in the phosphorus oxidation reaction, but that the chains are terminated by the walls of the vessel. The greater the gas pressure the smaller *relatively* is the effect of the walls, so that as the pressure is increased the condition is attained at which  $A(1 - a)$  exceeds  $f_s$ , and the reaction suddenly becomes very rapid. In harmony with this view it is found that with large vessels, in which the area/volume ratio is less than in small vessels, the rapid reaction stage is reached at lower pressures, since the de-activation effect is relatively less. In the same way the presence of argon lowers the critical pressure by preventing the active molecules from reaching the wall; in this manner the  $f_s$  factor is reduced. At higher pressures the effect of de-activation by non-elastic collisions in the gas phase increases, so that a pressure may be reached at which the combined effect of the now appreciable factor  $f_c$  and  $f_s$  exceed  $A(1 - a)$ . The reaction velocity should then fall suddenly to a very low value; this probably accounts for the fact that at pressures of 1 atm. and at ordinary temperatures phosphorus does not glow in oxygen, although it does at lower pressures.

Similar reactions with definite pressure limits between which a



mixture of gases is explosive have been obtained by Hinshelwood and by Semenov and their co-workers (1929 *et seq.*); examples are the combination of hydrogen, phosphine, carbon disulphide, and carbon monoxide, respectively, with oxygen. In each case the variation of reaction velocity with pressure may be represented by curves of the type in Fig. 23. As the pressure is increased the reaction velocity increases slowly from A to B; at B the process suddenly becomes explosive and remains so over the pressure range BC. At C the velocity falls suddenly to a normal value, and then increases steadily until the point D, where a thermal explosion, *not* due to the propagation of an ever-increasing number of branched chains, occurs.

The combination of hydrogen and oxygen is, as already mentioned, a chain reaction, and it is believed that  $\text{H}_2\text{O}_2$  molecules or OH radicals are responsible for the initiation of the non-stationary chains (p. 312). At very low pressures the walls of the vessel cause de-activation at a greater rate than that of chain formation, that is  $f_s > A(1 - a)$ , and  $f_c$  is small. At the pressure represented by B, the sum of  $f_s + f_c$  is equal to  $A(1 - a)$  but opposite in sign, and the reaction becomes explosive; it remains so until the pressure is increased to C. Beyond this value the de-activation by collision,  $f_c$ , becomes relatively appreciable and once more  $f_s + f_c > A(1 - a)$ , and the reaction velocity is measurable.

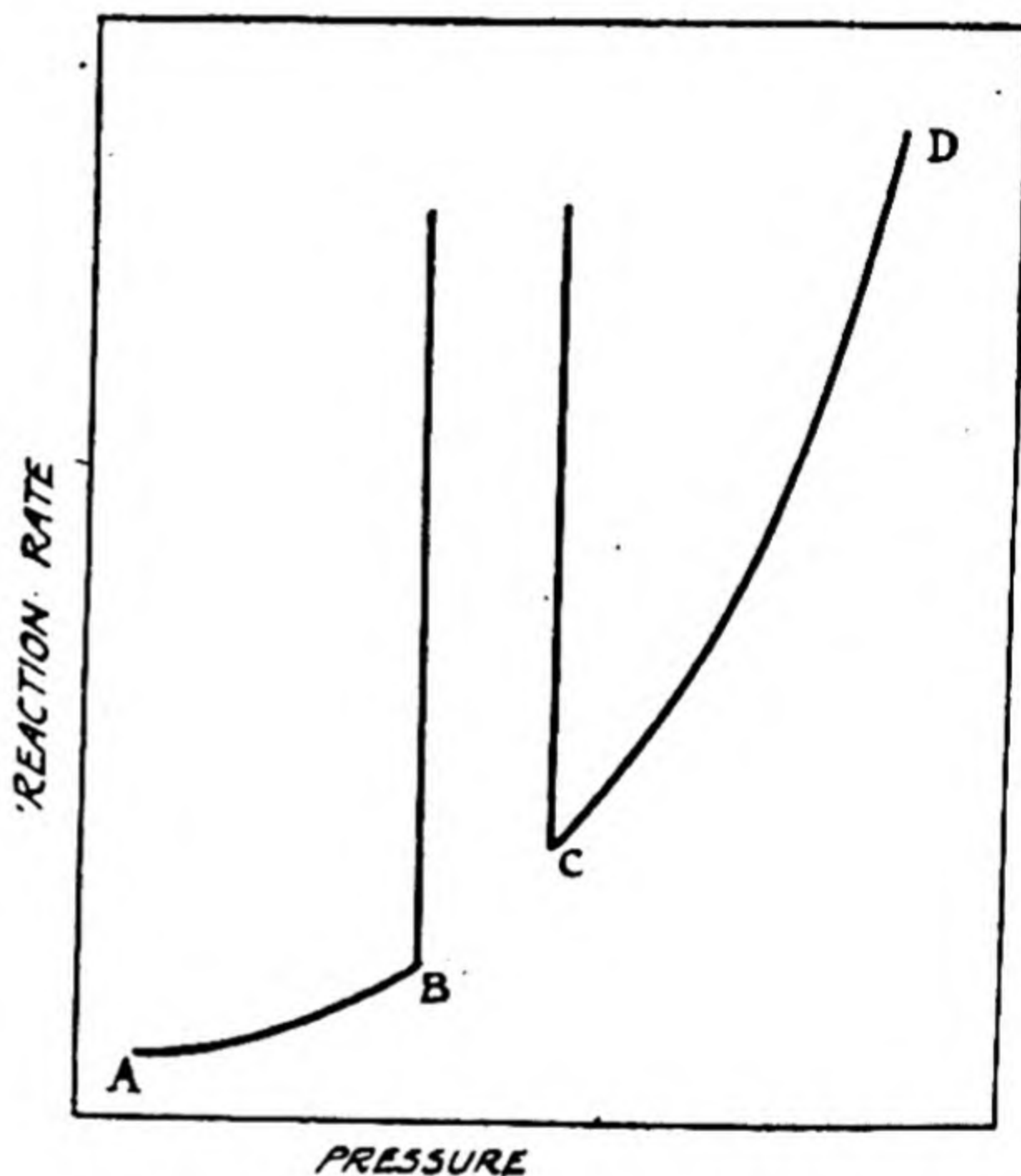
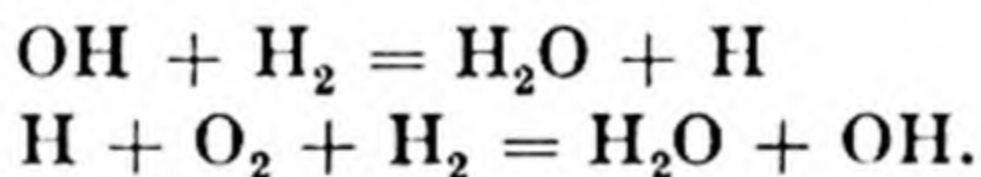


FIG. 23.—Variation of velocity with pressure in a reaction involving the propagation of non-stationary chains; between the pressure limits of B and C the reaction is explosive. (After Hinshelwood.)

**Origin of Reaction Chains.** Reference has been made to two

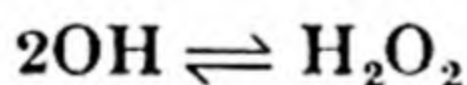


methods of initiating reaction chains, viz., by "hot" molecules or by atoms produced in the reaction, but there is a third, somewhat surprising, source of chains which is found in some processes. In the course of a study of the low pressure (50—200 mm.) reaction between hydrogen and oxygen at about 530° C. Alyea and Haber (1930) brought streams of the two gases through tubes at right angles to one another into the centre of a large spherical vessel; under these conditions only slight reaction occurred. On introducing a quartz rod, the temperature being below that of the gases, immediate explosion occurred and continued as long as the rod remained; a similar result was produced by glass, porcelain, copper or iron rods, but not by aluminium. The reaction is undoubtedly homogeneous and has a chain mechanism, and consequently the results of Alyea and Haber lead to the conclusion that the chains originate at the surface introduced; in the relatively small glass vessels used by Hinshelwood and Gibson (1928) and others the chains presumably started at the walls of the vessel. According to Alyea (1931) the hydrogen and oxygen gases adsorbed at low pressures react on the surface and send out OH radicals which start the chain mechanism, thus



The latter reaction probably occurs in two stages (Melville, 1934), the first involving the formation of  $\text{HO}_2$  in a three-body collision, and the second yielding water and hydroxyl radicals.

Garstang and Hinshelwood (1931) consider that hydrogen peroxide molecules are formed by the reaction of the gases at the surface and that these initiate chains, although the existence of the equilibrium



makes the two views not incompatible. The observation that in a silver vessel the reaction of hydrogen and oxygen is purely at the surface (Hinshelwood, Moelwyn-Hughes and Rolfe, 1933) may be significant; it is suggested that the surface of silver-silver oxide catalytically destroys the active species which normally propagates the reaction chains in the gas phase. The silver-silver oxide



surface would, of course, be an excellent catalyst for the decomposition of hydrogen peroxide.

The idea that reaction chains may be started, as well as broken, at surfaces has been extended to a number of other processes, *e.g.*, the oxidation of carbon disulphide (Thompson, 1930), and of carbon monoxide (Cosslett and Garner, 1931) and the reaction between ozone and hydrogen bromide (Lewis and Feitknecht, 1932), and it is now generally accepted as a third method for the initiation of chain processes. It explains satisfactorily the dependence of the rates of reaction in many instances on the state and nature of the surface of the vessel and on the presence of gas films. In some complex reactions, *e.g.*, the hydrogen and oxygen combination, it should be borne in mind that chains may originate in different ways under different conditions, and so changes in the kinetics of the process may be accounted for.

In developing the theory of the origin of reaction chains at surfaces Alyea suggested that the sudden reduction in the velocity of the hydrogen-oxygen reaction above a certain critical pressure was due to the fact that the surface, at this pressure, was completely covered by hydrogen to the exclusion of oxygen. Under these conditions it is supposed that hydrogen atoms are sent out at a slow rate, but no hydroxyl radicals, and consequently there is a sudden change in the nature of the reaction; the same explanation is supposed to apply to other cases of a similar type. This theory of the upper critical pressure has, however, met with much opposition. Garstang and Hinshelwood (1931) showed that the introduction of excess of either hydrogen or oxygen will suppress the low pressure explosion, and so the change, if any, in the adsorbed layer cannot be that postulated by Alyea. Further, a study of the heterogeneous combination of hydrogen and oxygen on silica has revealed the fact that under the conditions of the upper critical pressure limit the surface is almost entirely covered with oxygen and only sparsely with hydrogen. Hinshelwood (1932) in reviewing the subject finds no reason to discard the view that the upper limit is due to the breaking of chains in the gas phase. Williamson (1933) has found that a surface takes several days to become completely covered with hydrogen, whereas the



upper explosion limit may be obtained within a few seconds of introducing the gas, in spite of the fact that the surface can only be covered to a minute extent.

The results obtained in the deuterium–oxygen reaction (Hinshelwood *et al.*, 1934; Frost and Alyea, 1934) support the accepted views concerning the explosion limits in the hydrogen–oxygen reaction. The lower limit is the same for the two isotopes, but the upper pressure limit is 1.3 times as great for deuterium as for hydrogen. If the chain carriers are OH and OD, respectively, they will reach the walls at almost equal rates, and so the lower limit should be unaffected, but since the  $D_2$  molecules move more slowly than those of  $H_2$ , the former will be less efficient as chain-breakers in the gas phase: for further consideration of the deuterium–oxygen reaction, see “Recent Advances in General Chemistry,” Chapter IV.

Melville and Roxburgh (1933) have obtained evidence that in the phosphine–oxygen reaction, at least, the upper critical limit is due to the breaking of chains in the gas phase. They studied the reaction with chains initiated by optically excited mercury atoms, and found that with increasing oxygen pressure the rate of reaction increases at first, then reaches a maximum and decreases. Allowing for the increased rate of de-activation of the mercury atoms by collision with oxygen molecules, the results show that the chain length decreases with increasing oxygen pressure. The view that chains are broken by collisions in the gas phase thus appears to be substantiated. Inert gases depress the lower critical explosion limit of the phosphine–oxygen reaction (Gray and Melville, 1935); the results are in harmony with the view that at low pressures the reaction chains are broken at the walls of the vessel. The molecules of inert gas prevent the access of the chain carriers to the walls, and so the lower the pressure at which explosion occurs.

### NEGATIVE CATALYSIS

**Inhibition.** Interesting evidence concerning the existence of reaction chains has been obtained in connection with the study of



negative catalysis. In 1924 Christiansen suggested that a negative catalyst, or inhibitor, acts either by breaking, or preventing the formation of, reaction chains. If the chains are of considerable length, involving as they sometimes do many thousands of molecules in successive links, then each molecule of inhibitor by removing the energy from the initiator of a chain right at the commencement is able to retard the reaction very considerably. Bäckström (1927) studied the photochemical oxidation of benzaldehyde, heptaldehyde and sodium sulphite solutions by means of gaseous oxygen, and concluded from the yields obtained that the processes involved chain reactions. The presence of very small traces, about one part in ten-thousand, of inhibitors, *e.g.*, anthracene and diphenylamine for benzaldehyde,  $\alpha$ - and  $\beta$ -naphthol for heptaldehyde, and various alcohols for sodium sulphite, markedly reduces the rate of photochemical reaction, and hence the length of the chains. It appears, therefore, that in the photochemical oxidation the negative catalysts are able to prevent the formation or development of chains. The important observation was then made that these inhibitors reduce the rate of the oxidation reactions occurring *in the dark* as purely thermal processes to the same extent as they affect the photochemical reactions. It may be inferred, in agreement with the theory of Christiansen, that in the thermal oxidations the negative catalysts act by breaking reaction chains. In a subsequent study Bäckström and Alyea (1929) investigated in more detail the inhibiting effect of iso-propyl, sec-butyl and benzyl alcohols on the oxidation of sulphite solutions. It was found that oxidation of the sulphite induced simultaneous oxidation of the alcohols to acetone, methyl ethyl ketone and benzaldehyde respectively; the amount of oxidation product was calculated to be two molecules for every chain broken. From this result it may be concluded that the alcohol molecules break the chains involved in the oxidation of sulphite by becoming oxidised themselves. Although these results were obtained for reactions involving liquids the conclusions concerning the mechanism of negative catalysis are of importance in connection with certain gas reactions. The breaking of chains is, however, not always the cause of negative catalysis; in some



cases the negative catalyst functions by reacting with, and so removing, a positive catalyst which is already present. The possibility of this alternative mechanism must, therefore, always be taken into consideration in the study of negative catalysis.

## REFERENCES

- ALYEA. *J. Amer. Chem. Soc.*, 1931, 53, 1324 ; 1933, 55, 3227.  
 ALYEA and HABER. *Z. physikal. Chem.*, 1930, B10, 193.  
 AMDUR. *J. Amer. Chem. Soc.*, 1935, 57, 856.  
 BÄCKSTRÖM *et al.* *Ibid.*, 1927, 49, 1460 ; 1929, 51, 50 ; *Trans. Faraday Soc.*, 1928, 24, 601.  
 BAWN. *Ibid.*, 1935, 31, 1536 ; 1936, 32, 178.  
 BOWEN. *Ann. Reports*, 1934, 31, 46.  
 BUSSE and DANIELS. *J. Amer. Chem. Soc.*, 1927, 49, 1257.  
 CHARITON and WALTA. *Z. Physik*, 1926, 39, 547.  
 CHRISTIANSEN. *J. Physical Chem.*, 1924, 28, 145.  
 CHRISTIANSEN and KRAMERS. *Z. physikal. Chem.*, 1923, 104, 451.  
 CLUSIUS. "Kettenreaktionen," 1932\*.  
 COFFIN. *Canad. J. Res.*, 1931, 5, 636 ; 1932, 6, 417 ; 7, 75.  
 COSSLETT and GARNER. *Trans. Faraday Soc.*, 1931, 27, 176.  
 DALTON. *Proc. Roy. Soc.*, 1930, 128A, 263.  
 Discussion on Energy Distribution in Molecules in Relation to Chemical Action, *Ibid.*, 1934, 146A, 239.  
 Discussion on the Critical Increment of Homogeneous Gas Reaction. *Chem. Soc.*, December 7th, 1931\*.  
 EYRING *et al.* *Z. physikal. Chem.*, 1929, B7, 244 ; 1931, B12, 279 ; *J. Amer. Chem. Soc.*, 1930, 52, 1472, 1486 ; 1931, 53, 2537 ; 1932, 54, 3191, 3876 ; 1934, 56, 2020 ; 1935, 57, 985, 1536 ; *J. Chem. Physics*, 1933, 1, 586 ; 1935, 3, 107 ; 1936, 4, 170.  
 FARKAS. "Orthohydrogen, Parahydrogen and Heavy Hydrogen," 1935\*.  
 FARKAS (L.) and WIGNER. *Trans. Faraday Soc.*, 1936, 32, 708.  
 FOWLER and RIDEAL. *Proc. Roy. Soc.*, 1927, 113A, 570.  
 FRANCK *et al.* *Z. Elektrochem.*, 1930, 36, 794 ; *Z. physikal. Chem.*, 1933, B20, 460.  
 GARNER and WILLAVOYS. *Trans. Faraday Soc.*, 1935, 31, 805.  
 HIBBEN. *J. Amer. Chem. Soc.*, 1928, 50, 937.  
 HINSHELWOOD *et al.* *Phil. Mag.*, 1925, 50, 860, 1135 ; *J. Chem. Soc.*, 1923, 123, 2730 ; 1924, 125, 893, 1841 ; 1925, 127, 327, 1552, 2896 ; 1926, 730 ; 1929, 1804 ; 1935, 1111 ; 1936, 371, 378 ; *Proc. Roy. Soc.*, 1924, 106A, 284 ; 1925, 108A, 211 ; 1926, 111A, 245, 380 ; 113A, 221, 230 ; 1927, 114A, 84 ; 115A, 215 ; 116A, 163 ; 117A, 131 ; 1928, 118A, 170 ; 119A, 591 ; 121A, 147 ; 1929, 122A, 610 ; 124A, 219 ; 125A, 277, 294 ; 1930, 127A, 218 ; 128A, 75, 88 ; 129A, 284 ; 1931, 130A, 640 ; 131A, 177 ; 134A, 1 ; 1932, 137A, 87 ; 138A, 297, 311 ; 1933, 139A, 521 ; 141A, 41 ; 142A, 77 ; 1934, 147A, 48 ; 1935, 149A, 340, 855 ; *Trans. Faraday Soc.*, 1928, 24, 545, 552 ; 1932, 28, 184 ; *Z. physikal. Chem.*, 1930, B10, 157 ; *Ann. Reports*, 1930, 27, 18, 41\* ; 1931, 28, 19\*, 41\* ; 1932, 29, 39\* ; 1933, 30, 89\* ; "Kinetics of Chemical Change in Gaseous Systems," 1934\*.  
 HUNTER. *Proc. Roy. Soc.*, 1934, 144A, 386.  
 JOST. *Z. Elektrochem.*, 1935, 41, 183, 232\*.  
 JOST and JUNG. *Z. physikal. Chem.*, 1929, B3, 83.



- KASSEL. *J. Physical Chem.*, 1928, 32, 225, 1065 ; 1930, 34, 1166, 1777 ; *Z. physikal. Chem.*, 1929, B2, 264 ; *J. Amer. Chem. Soc.*, 1928, 50, 1344 ; 1929, 51, 54 ; 1932, 54, 3949 ; "Kinetics of Homogeneous Gas Reactions," 1932.\*
- KISTIAKOWSKY & al. *J. Amer. Chem. Soc.*, 1930, 52, 3785, 4837 ; *Z. physikal. Chem.*, 1931, Bodenstein Festband, 369.
- KOWALSKY. *Z. physikal. Chem.*, 1929, B2, 288.
- LENHER. *J. Amer. Chem. Soc.*, 1931, 53, 3737, 3752.
- LESSIG. *J. Physical Chem.*, 1932, 36, 2325.
- LEWIS, B. *J. Amer. Chem. Soc.*, 1930, 52, 3120.
- LEWIS, B. and Feitknecht. *Ibid.*, 1932, 54, 1790.
- LEWIS, G. N. and SMITH. *Ibid.*, 1925, 47, 1508.
- LINDEMANN. *Trans. Faraday Soc.*, 1922, 17, 598.
- LINHORST and HODGES. *J. Amer. Chem. Soc.*, 1934, 56, 836.
- LUECK. *Ibid.*, 1922, 44, 757.
- MELVILLE et al. *Proc. Roy. Soc.*, 1931, 132A, 108 ; 1934, 146A, 737, 760 ; *Trans. Faraday Soc.*, 1932, 28, 308, 814 ; 1935, 31, 452 ; *J. Chem. Soc.*, 1934, 1246.
- MOELWYN-HUGHES. *Ann. Reports*, 1935, 32, 89\*.
- NERNST. *Z. Elektrochem.*, 1918, 24, 335.
- PATAT. *Ibid.*, 1936, 42, 85\*, 265\*.
- PEASE. *J. Amer. Chem. Soc.*, 1931, 53, 613 ; 1932, 54, 1876.
- PELZER and WIGNER. *Z. physikal. Chem.*, 1932, B15, 445.
- POLANYI et al. *Z. Elektrochem.*, 1927, 33, 554 ; *Trans. Faraday Soc.*, 1928, 24, 606 ; 1934, 30, 519 ; 1935, 31, 875 ; *Z. physikal. Chem.*, 1928, B1, 3, 21, 30, 62 ; 1930, B11, 97, 291, 316 ; 1932, B17, 220 ; B19, 139 ; "Atomic Reactions," 1932\*.
- RAMSPERGER et al. *J. Amer. Chem. Soc.*, 1927, 49, 912, 1495 ; 1928, 50, 714 ; 1929, 51, 918, 2134 ; 1931, 53, 2061 ; 1933, 55, 214 ; *J. Physical Chem.*, 1930, 34, 669 ; *Chem. Reviews*, 1932, 10, 38\*.
- RICE et al. *J. Physical Chem.*, 1927, 31, 1572 ; *J. Amer. Chem. Soc.*, 1927, 49, 1617 ; 1928, 50, 617, 2042 ; 1930, 52, 95 ; 1934, 56, 1444 ; 1935, 57, 310, 1384 ; *J. Chem. Physics*, 1934, 2, 853 ; 1935, 3, 479.
- RICE (F. O.) and HERZFELD. *J. Amer. Chem. Soc.*, 1934, 56, 284.
- RIESENFELD and SCHUMACHER. *Z. physikal. Chem.*, 1928, 138, 268.
- SCHAY. "Hochverdünnte Flammen," 1930\*.
- SCHUMACHER and SPRENGER. *Proc. Nat. Acad. Sci.*, 1930, 16, 129 ; *Z. physikal. Chem.*, 1931, B12, 115.
- SEMENOFF. *Z. Physik*, 1927, 46, 109 ; *Z. physikal. Chem.*, 1929, B2, 169 ; 1930, B6, 307 ; *Chem. Reviews*, 1929, 4, 347\* ; *Trans. Faraday Soc.*, 1932, 28, 818 ; 1933, 29, 606 ; "Chemical Kinetics and Chain Reactions," 1935\*.
- SHERMAN and SUN. *J. Amer. Chem. Soc.*, 1934, 56, 1096.
- SPRENGER. *Z. physikal. Chem.*, 1928, 136, 49.
- STEACIE et al. *J. Chem. Physics*, 1933, 1, 618 ; 1934, 2, 345, 503 ; 1936, 4, 220.
- Symposium on Kinetics of Homogeneous Gas Reactions. *Chem. Reviews*, 1932, 10, 1-264\*.
- Symposium on the Kinetics of Reaction. *Ibid.*, 1935, 17, 43-88\*.
- TAYLOR, H. A. et al. *J. Physical Chem.*, 1929, 33, 1793 ; 1930, 34, 2761 ; 1931, 35, 2658, 2676 ; 1932, 36, 670, 1051 ; *J. Chem. Physics*, 1936, 4, 211.
- TAYLOR, H. S. *Chem. Reviews*, 1931, 9, 1\*.
- THOMPSON et al. *Z. physikal. Chem.*, 1930, B10, 273 ; 1931, B14, 359 ; *J. Physical Chem.*, 1931, 35, 3639 ; *J. Chem. Soc.*, 1931, 1809 ; 1932, 933 ; 1933, 1231 ; *Trans. Faraday Soc.*, 1932, 28, 299.



- TOLMAN *et al.* *J. Amer. Chem. Soc.*, 1925, 47, 1240, 1524 ; 1927, 49, 1183, 1202, 1650.  
VAUGHAN. *Ibid.*, 1932, 54, 3863 ; 1933, 55, 4109.  
VERNON and DANIELS. *Ibid.*, 1933, 55, 922.  
VOLMER *et al.* *Z. physikal Chem.*, 1930, B10, 141, 414 ; 1932, B19, 85 ; 1933, B21, 257 ; 1934, B25, 81.  
WILLIAMSON. *J. Amer. Chem. Soc.*, 1933, 55, 1437.  
WILLEY. *J. Chem. Soc.*, 1930, 336.

\* Review papers and books, wherein further references are to be found, are marked by an asterisk.



## CHAPTER VI

## PHOTOCHEMICAL REACTIONS

THE subject of photochemistry has advanced so rapidly in recent years that it is impossible to give an adequate account of the progress in the short space available ; three aspects only, which have helped very considerably in the elucidation of the mechanism of photochemical reactions, will be chosen for special treatment here. These are firstly the law of photochemical equivalence, usually associated with the name of Einstein, secondly the application of knowledge derived from a study of band spectra (Chapter IV.), and thirdly a study of the kinetics of the process.

## THE LAW OF PHOTOCHEMICAL EQUIVALENCE

**The Quantum Efficiency.** Although the idea of photochemical equivalence was first put forward by Stark (1905) its influence in photochemistry was not felt until the law was proved thermodynamically by Einstein in 1912, and subsequently (1918) deduced by him on quite different theoretical grounds. According to this law each molecule taking part in a photochemical process absorbs one quantum of the radiation causing the reaction or, in other words, each quantum absorbed brings about the decomposition of one molecule. If  $\nu$  is the frequency of this radiation, then the value of the corresponding quantum is  $h\nu$ , and  $Nh\nu$  should be equal to the radiant energy ( $U$ ) absorbed by 1 gm. mol., where  $N$  is the Avogadro number; thus

[illegible]

[illegible]

where  $c$  is the velocity of light, and  $\lambda$  the wavelength of the absorbed radiation. Since  $h$  is equal to  $6.547 \times 10^{-27}$  erg secs.,  $N$  is  $6.062 \times 10^{23}$ , and  $c$  is  $3 \times 10^{10}$  cm. per sec.,

$$U = 2.844 \times 10^8 / \lambda \text{ cals. per gm. mol, . . . (i.c)}$$



if  $\lambda$  is expressed in Ångström units ( $10^{-8}$  cm.). The number of gm. mols. of reactant which should decompose for each calorie of absorbed radiation, according to the law of the photochemical equivalent, is given the symbol  $p$  and may be represented by

$$p = \frac{1}{U} = \frac{\lambda}{2.844 \times 10^8} \text{ gm. mols.} \quad . \quad . \quad . \quad . \quad (ii.)$$

The actual experimental value of the number of gm. mols. decomposing is called  $\phi$ , and the ratio of  $\phi/p$ , represented by  $\gamma$ , is the "quantum efficiency" of the reaction. This term indicates the actual number of molecules decomposed for each quantum of absorbed radiation; if the Einstein law held exactly then  $\gamma$  should always be equal to unity. Incidentally it follows, from the law of photochemical equivalence, that the velocity of a purely photochemical process, involving no thermal or "dark" reaction, should be independent of temperature, except in so far as the latter affects the absorption capacity for radiation of the reacting system. If each quantum absorbed causes one molecule to decompose it is clear that temperature can otherwise have no effect on the rate of reaction.

Since 1912 many photochemical changes have been studied quantitatively; the reacting system is exposed to appropriate radiation of known wavelength, and by means of a suitable radiometer the quantity of energy absorbed is measured. At the same time the extent of the chemical reaction is determined, and so the number of molecules decomposed per quantum of light absorbed, *i.e.*, the quantum efficiency, is calculated. The value of  $\gamma$  is rarely equal to unity, but this would perhaps be so if the reaction involved *one molecule only* in each act of decomposition; as such reactions are probably uncommon, it is generally considered that the law of photochemical equivalence is obeyed if the quantum efficiency is approximately equal to any integer up to three. Using this criterion Bowen and Watts in 1926 concluded, from an examination of published data, that 65 per cent. of the reactions which had been studied up to that time were in harmony with the equivalence law; the results reported since that date would probably increase this proportion. In Table LIX. are given



a few values of the quantum efficiency ( $\gamma$ ) which may be regarded as being in accordance with the law.

TABLE LIX.—*Quantum Efficiencies of Photochemical Reactions*

Reaction.	$\lambda$ (Å).	$\gamma$
Decomposition of—		
Hydrogen iodide . . .	2090—2530	2.0—2.1
Hydrogen bromide . . .	2070—2820	1.97—2.08
Nitrosyl chloride . . .	3650—6300	2.1
Ozone (+ chlorine) . . .	4200	ca. 2
Chlorine monoxide . . .	4600	2.1—2.5
Chlorine dioxide in $\text{CCl}_4$ . . .	3000—4000	2.0—2.2
$3\text{O}_2 \rightarrow 2\text{O}_3$ . . . . .	2090	3.1
$\text{Br}_2 + \text{C}_6\text{H}_{12}$ . . . . .	4700	ca. 1
$\text{Fe}^{++} + \text{I}_2$ . . . . .	5790	1
<i>o</i> -Nitrobenzaldehyde $\rightarrow$ . . . <i>o</i> -nitrosobenzoic acid.	Violet	1
Hydrolysis of chloroacetic acid . . .	2540	1
Polymerisation of cyanogen . . .	2145—2240	ca. 3

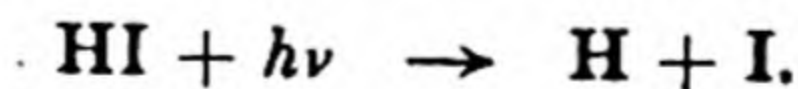
In other cases, however, the results appear to diverge in a very marked manner from the requirements of the idea of photochemical equivalence; for example, in the union of moist hydrogen and chlorine the quantum efficiency is of the order of  $10^6$  molecules reacting per quantum of absorbed radiation. This is an exceptionally high efficiency, but there are many instances of values of  $\gamma$  which are of the order of several hundred molecules per quantum. On the other hand, in some reactions many quanta are required to bring about the decomposition of a single molecule; for example, Warburg (1919) has found that when a 0.01 molar solution of maleic acid is exposed to ultra-violet radiation of wavelength 2070 to 2820 Å, it is converted into fumaric acid, but the quantum efficiency is only about 0.03 to 0.04. It would appear, therefore, that the law of photochemical equivalence is only approximately applicable in a limited number of cases, but further consideration will show that this opinion must probably be revised to include all reactions within the law.

**Conditions of Applicability of the Einstein Law.** Allmand (1925)



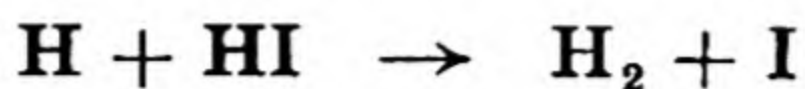
has made a careful analysis of the theoretical basis of the Einstein law, and has concluded that it can hold rigidly only under the following conditions: (a) all the reacting molecules should be at the same energy level before reacting, and hence equally reactive; (b) the reactivity of the absorbing molecules under a given radiation density must be independent of temperature; (c) the amount of energy absorbed per absorbing molecule should be the same in every case and also independent of temperature; and (d) the product after the absorption of energy must be fundamentally unstable with respect to the original absorbing system, and should revert to the latter at a rate independent of temperature. If these stipulations hold, then the process occurring is the same for every molecule of the reacting substance, and the whole system should obey the equivalence law. Any departure from the theoretical conditions will cause a deviation from the requirements of the law, but such deviations will in general be small and by no means sufficient to account for the very high and low quantum efficiencies to which reference has already been made.

It was emphasised, however, by Stark (1912) that the equivalence law could only be expected to apply to the *primary* photochemical reaction; this might be succeeded by secondary processes with the result that the primary quantum efficiency of the absorbed radiation would be completely obscured. If the secondary reaction is connected in a simple stoicheiometric manner with the primary stage initiated by the absorbed light, then the quantum efficiency will be a simple whole number, *e.g.*, one, two or three. The reactions quoted in Table LIX. are evidently of this type, and subsequently the mechanism of certain of these cases will be discussed in detail; although the quantum is absorbed by only one reacting molecule the total number of molecules decomposed as a result of secondary reactions may be two or more. For example, in the photochemical dissociation of hydrogen iodide the primary process is the absorption of one quantum of radiation by a molecule of hydrogen iodide, in accordance with the equivalence law. As a result of this access of energy the molecule decomposes into a hydrogen and an iodine atom, thus

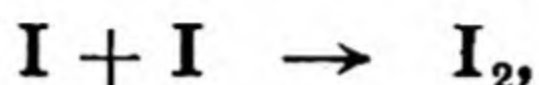




This is followed by the secondary reactions, which are purely thermal or "dark" processes,



and



so that the *net* result is the decomposition of two molecules of hydrogen iodide per single absorbed quantum. The apparent quantum efficiency of the total reaction is thus two, although it is actually unity, in accordance with the Einstein law, in the primary process.

**High Quantum Efficiencies.** When the quantum efficiency of a reaction is very large, *e.g.*, in the photochemical union of hydrogen and chlorine, it is most probable that reaction chains are set up as a result of the primary processes initiated by radiation. The particular case of the hydrogen-chlorine combination has been already mentioned in Chapter V., and there is very little doubt that in this reaction a chain mechanism is operative. The primary process is probably the absorption of one quantum of radiation by a single molecule of chlorine, which either directly or as the result of a collision dissociates into atoms; these initiate a series of reaction chains, able to continue in the dark (see p. 303), so that the total amount of hydrogen and chlorine combining is greatly in excess of the number of molecules of the latter absorbing radiation. Evidence that the law of quantum equivalence is applicable to the primary reaction even in such cases where a chain process follows the initial photochemical reaction has been obtained in a number of ways. Lind and his co-workers (1980) have compared the rates of certain photochemical reactions with high quantum yields with the reactions, under the same conditions, induced by  $\alpha$ -particles; in the hydrogen-chlorine, carbon monoxide-chlorine reactions, and in the oxidation of sodium sulphite by oxygen the yield per quantum was almost identical with the yield per ion-pair produced by the  $\alpha$ -particles. Incidentally in the hydrogen-chlorine combination the temperature coefficient was the same in both cases. Since in the primary process with  $\alpha$ -particles one ion-pair probably stimulates one molecule to react, it is reasonable to suppose that in the photochemical reaction the



first stage involved is the absorption of a single quantum by one molecule of reactant.

In the oxidation of sulphite solutions in the presence of alcohols as inhibitors chain reactions occur (p. 815), but quantitative measurements show that the primary reaction probably obeys the law of photochemical equivalence. Bäckström and Alyea (1929) have found that for the photochemical oxidation of a solution which is 0.1 molar with respect to benzyl alcohol, the quantum yield is 128 molecules of sulphite oxidised per quantum of absorbed radiation; at the same time it was observed that 58 molecules of sulphite were oxidised for every one molecule of alcohol, indicating that the chain following the primary photochemical process was 58 molecules in length (see p. 805). It follows, therefore, that each quantum of radiation initiates  $128/58 = 2.2$ , or within the limits of experimental error 2, reaction chains; this implies a quantum efficiency of two in the primary process. If it is assumed that two molecules of alcohol are oxidised when a reaction chain is broken, then the quantum efficiency becomes unity. It is clear, therefore, that even for such a complicated reaction as the inhibited oxidation of sulphite solutions the results can be brought into line with the law of photochemical equivalence. Similar results have been obtained by Cremer (1927) in connection with the hydrogen-chlorine reaction in the presence of oxygen as inhibitor.

**Low Quantum Efficiencies.** In the reactions of low quantum efficiency it appears that a molecule having absorbed a quantum of radiation is deprived of all or part of that energy before it has an opportunity to react. The molecule may re-radiate some of its absorbed energy at a lower frequency, so that it is reduced to a lower energy level in which its chances of reaction are greatly decreased. Alternatively it may collide with another atom, or molecule, *i.e.*, a so-called "inelastic collision," so that the electronic energy of the activated molecule is transferred into kinetic energy of translation, and thus is prevented from undergoing photochemical decomposition or reaction. In this manner it is clear that although one molecule may absorb one quantum of energy the chances of that molecule reacting may be very small, so that



many quanta must be absorbed for each decomposing molecule ; the quantum efficiency of the reaction will then be very low, although fundamentally the Einstein law is obeyed. At the present time, therefore, the law of photochemical equivalence is generally accepted as applying to the primary process of a reaction occurring under the influence of radiation ; the use of this conception has proved of great value in the elucidation of the mechanism in many photochemical reactions.

**Evidence for the Einstein Law.** The introduction of the quantum idea into photochemistry has undoubtedly helped to co-ordinate results which would at first sight have appeared somewhat perplexing. For example, Warburg (1918) found that in the decomposition of hydrogen iodide in ultra-violet light of wavelengths 2070, 2530 and 2820 Å the number of gm. atoms of iodine produced per gm. calorie of absorbed radiation was as follows :

Wavelength in Å	2070	2530	2820
Gm. atoms of iodine $\times 10^5$ /calorie	1.44	1.85	2.09

There seems to be no relationship between these results, but if the figures are recalculated in order to give the number of atoms produced per *quantum* of absorbed radiation the values are 1.98, 2.08 and 2.10, respectively ; within the limits of experimental error these correspond to a quantum efficiency of two over the whole range of wavelengths studied. It might be thought that this value is a matter of chance, but this is not so : its fundamental significance is shown by the fact that the quantum efficiency is the same in liquid hydrogen iodide, for the gas at temperatures of 150° to 175° (Bodenstein and Lieneweg, 1926), and at pressures as low as 0.1 mm. of mercury (Lewis, 1927). These results offer very convincing support for the view that photochemical reactions involve a quantum mechanism.

Evidence in the same direction has been obtained from experiments of a different type : when mercury vapour is exposed to the light from a mercury vapour lamp the former emits a " resonance line " with a wavelength of 2536 Å (1 quantum  $\equiv$  112,000 cals. per gm. mol.); this radiation can be quenched if various gases are added to the mercury vapour, and in this connection



hydrogen is particularly effective. In 1921 Cario and Franck observed that if a little mercury vapour was mixed with hydrogen and exposed to the light of a mercury lamp the hydrogen became very active chemically; subsequently Taylor, and others, investigated the properties of the gas and found that it combined readily with oxygen, reduced ethylene to ethane, carbon monoxide to formaldehyde, and in fact behaved exactly like atomic hydrogen.

The mercury atoms are excited by exposure to radiation to such an extent that they are able to emit a radiation of 2536 Å on returning to their normal state, but if other molecules are present the excited mercury atoms are able to transfer their excess energy to them; if this energy is passed as a single quantum it is equivalent to the transfer of 112,000 calories per gm. mol. The heat of dissociation of hydrogen is about 100,000 calories per gm. mol., and so it is in favour of the quantum theory to find that excited mercury atoms are able to bring about this dissociation. Cadmium vapour has a similar resonance line at 3262 Å, but although the radiation is quenched by hydrogen gas the molecules are not dissociated, and the gas has no exceptional chemical activity. The excitation energy corresponding to the 3262 Å line is, on the basis of the quantum theory, 88,000 calories per gm. mol., and so is not sufficient to bring about the dissociation of hydrogen molecules. The latter, however, have a vibrational level in the ground state, the excess energy of which corresponds approximately with this value (3.84 volts, as compared with 3.78 volts as the energy level of the excited cadmium atom); it appears, therefore, that when hydrogen quenches the resonance radiation of cadmium, the former is merely raised to a higher vibrational energy level. These observations on the photo-activity of resonance radiation support the view that a quantum mechanism is operative in photochemical processes.

### APPLICATION OF MOLECULAR SPECTRA

**Discontinuous Spectra.** In Chapter IV. it has been shown that when a molecule absorbs radiation there may be changes in the rotational, vibrational and electronic energy levels. Purely rotational changes are brought about by radiations of long wavelength,



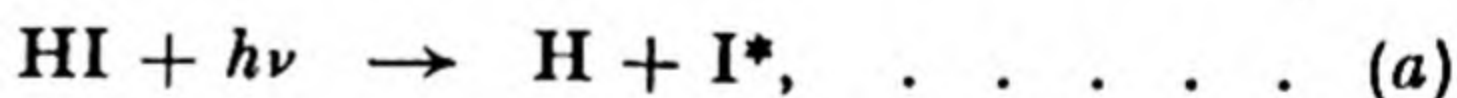
namely those in the far infra-red, but as rotational changes are rarely able to bring about decomposition or appreciable activation of a molecule such radiations are not photochemically active. Vibrational changes, if sufficiently great, could bring about dissociation of a molecule, but when purely vibrational transitions occur it is known that the quantum number changes only by very small amounts, generally not more than three units (p. 321); it is very improbable, therefore, that radiations in the near infra-red, such as are responsible for vibrational changes, will be effective in bringing about chemical reactions. When absorption occurs in the ultra-violet or violet regions of the spectrum the molecule suffers an electronic change, with the result that it may become so activated as to decompose on collision with another molecule; under such conditions the electronic band spectrum of the absorbing molecule retains its vibrational and rotational fine structure. If the vibrational bands only are present, and the rotational structure is diffuse, as in the so-called "pre-dissociation spectra" (p. 229), the molecule absorbing the radiation dissociates spontaneously within a very short time of receiving the energy quantum.

**Continuous Spectra.** In some cases, *e.g.*, iodine, the electronic absorption spectrum becomes continuous at a certain wavelength; this means that simultaneously with the electronic change the molecule undergoes a vibrational change of sufficient energy to bring about dissociation. It does not follow always that the absorption of a quantum of energy larger than the heat of dissociation of the molecule will result in its dissociation. For example, it has been found (Oldenberg, 1923) that molecular iodine vapour can absorb and emit radiation bands in the vicinity of a wavelength of  $1900 \text{ \AA}$ ; the energy acquired by the molecule is about five times the amount required to bring about dissociation (p. 222), yet the fine structure of the bands indicates that no such dissociation occurs. The explanation of this behaviour is that although the electronic energy level is raised very considerably, the vibrational energy is not increased at the same time to a sufficient extent to allow the parts of the molecule to separate. Thus only from an examination of the type of absorption spectrum produced by any reacting molecule is it possible to determine

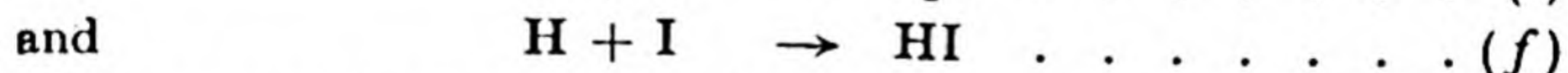
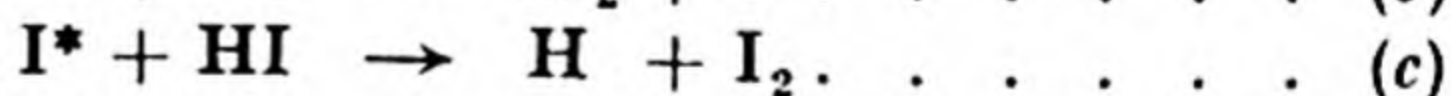
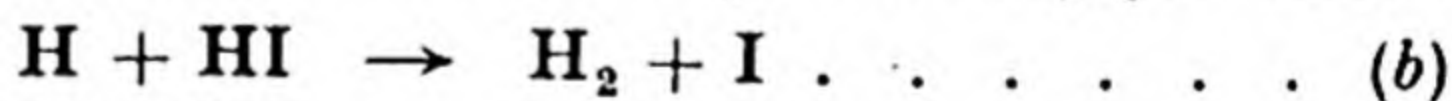


whether the primary photochemical process is activation of the molecule, that is raising it to a higher electronic level, or direct dissociation into atoms; the wavelength of the absorbed radiation alone is not a sufficient guide in this matter. It must be realised that the absorption of one quantum of radiation per molecule at a wavelength of about 2000 Å means that 1 gm. mol. of reactant acquires over 140,000 calories of energy; hence the effect of absorbing radiation in the violet or ultra-violet regions, even if it does not bring about dissociation, is undoubtedly to produce a very reactive molecule.

**Decomposition of Hydrogen Iodide.** The application of the photochemical equivalence law and the knowledge of band spectra to the elucidation of the mechanism of certain reactions will be illustrated by means of some examples. Hydrogen iodide shows continuous absorption in the ultra-violet region of the spectrum at wavelengths shorter than 3200 Å at least (*vide infra*), and hence it may be assumed that in this region it undergoes photochemical decomposition into atoms. The energy associated with the wavelength of 3200 Å is about 89,000 cal. per gm. mol., whereas the heat of dissociation of hydrogen iodide, into hydrogen and iodine atoms, is known to be about 68,000 cal.; the difference between the first and second electronic levels of iodine is 21,600 cal. (p. 222), and so it is probable that when hydrogen iodide is exposed to radiation of wavelength less than 3200 Å it decomposes thus



in agreement with the Einstein law. The products of the primary reaction may then take part in the following secondary processes:

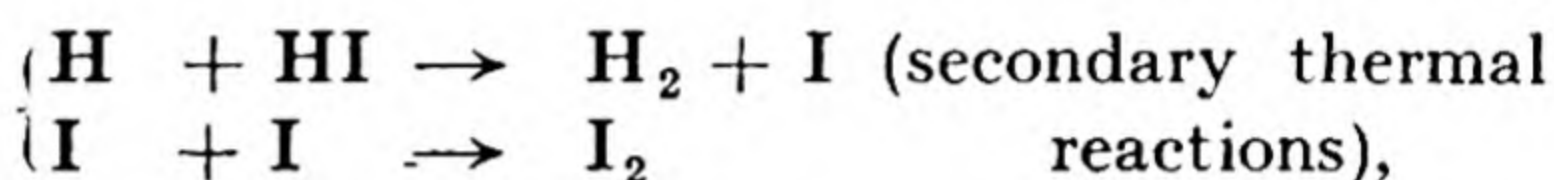
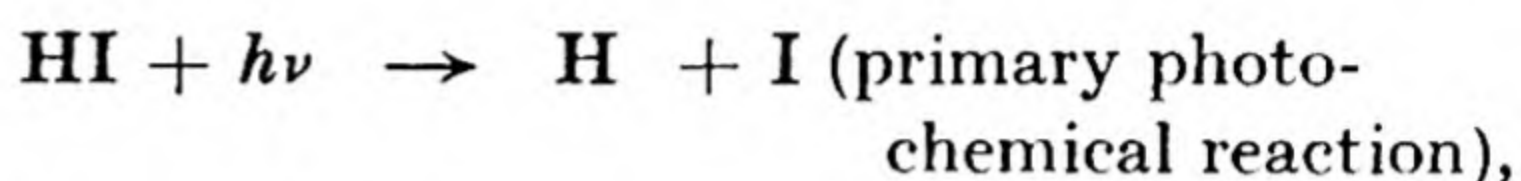


Of these reactions (c) is endothermic and so will not occur to any appreciable extent, whereas reactions (d) and (f) are so highly

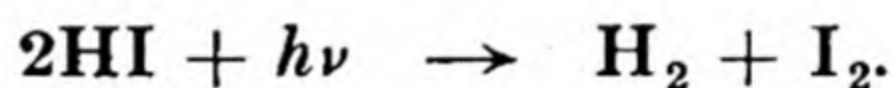
\* As in Chap. V. an asterisk is used to denote an activated molecule.



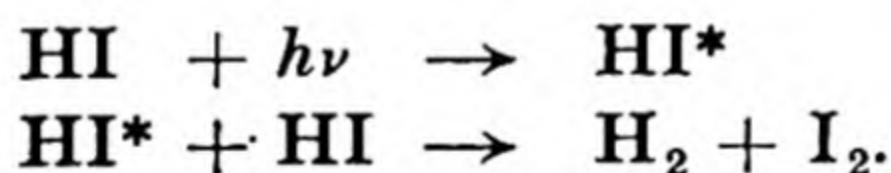
exothermic that the resulting molecules may dissociate immediately unless they can be relieved of some of their energy in a three-body collision or as a wall reaction (p. 284). It appears, therefore, that the hydrogen and iodine atoms resulting from the primary photochemical decomposition of the hydrogen iodide are removed by reactions (b) and (e), although the latter probably occurs only as a wall reaction or as a result of a three-body collision. The net reaction is consequently the decomposition of two molecules of hydrogen iodide for every quantum absorbed; the stages may be represented by



and together



It had been suggested at one time that an alternative mechanism of the process was the activation of the hydrogen iodide molecule by the absorption of a quantum of radiation, and that decomposition resulted when this molecule collided with another molecule, thus



Although this would account for the quantum efficiency it is ruled out by the continuous absorption spectrum of hydrogen iodide in the region of the photochemically active radiation; this indicates that primary decomposition, and not activation, occurs.

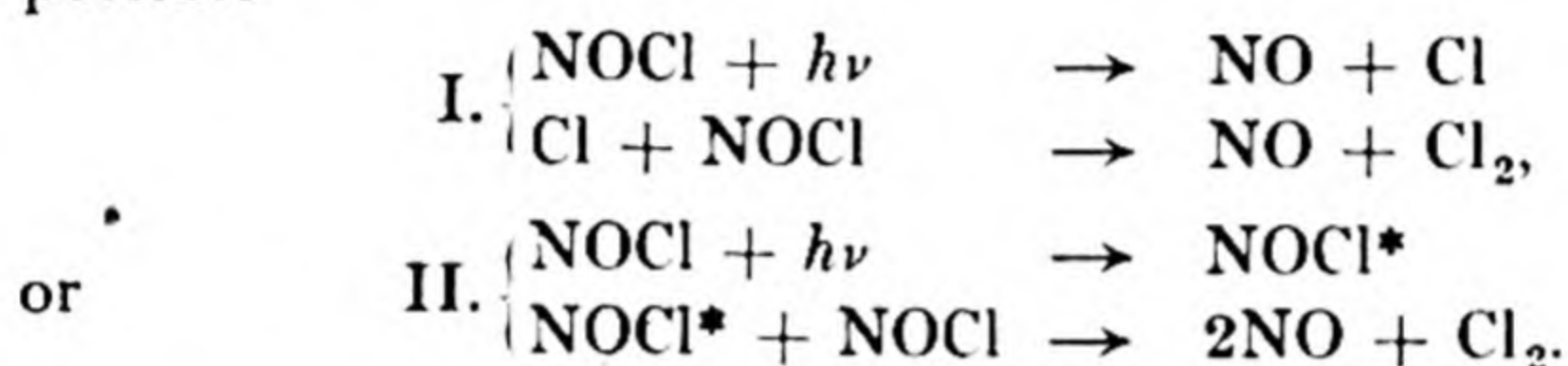
A careful investigation by Rollefson and Booher (1931) has shown that the region of continuous absorption in the spectrum of hydrogen iodide extends to 4000 Å; the quantum is then equivalent to about 70,000 cal., and so the products of dissociation between 3200 and 4000 Å must be normal atoms of both hydrogen and iodine. It has been observed that light of 4047 Å will bring about the decomposition of hydrogen iodide; the mechanism already discussed is clearly independent of whether the iodine atom is excited or not.

The decomposition of hydrogen bromide follows exactly the



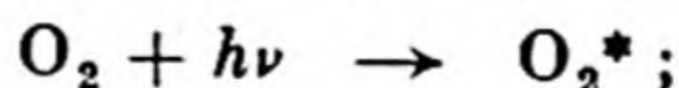
lines of hydrogen iodide; the spectrum of the former shows continuous absorption at wavelengths shorter than 2640 Å, and light of the same wavelength brings about decomposition, with a quantum efficiency of two molecules.

**Decomposition of Nitrosyl Chloride.** Kistiakowsky (1930) has made a careful study of the photochemical decomposition of nitrosyl chloride with radiations of wavelength 3650 to 6350 Å, and has found an almost constant efficiency of two molecules per quantum over this range; two mechanisms for the reaction seem possible



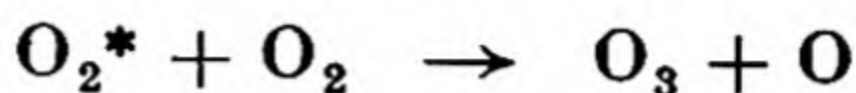
If mechanism I. were correct, the nitrosyl chloride should show continuous absorption in the spectral region studied, but for mechanism II. a band spectrum, with vibrational and rotational structure, would be expected. Experimental observation has shown a series of bands from 5990 down to less than 2500 Å units, all of which possess distinct line structure, and so mechanism II. is probably correct. Another point in favour of this mechanism is that the minimum dissociation energy, assuming neither of the products is in the excited state, is 46,400 cal. per gm. mol.; this corresponds to a wavelength of 6180 Å, whereas actually light of 6400 Å wavelength (44,300 cal.) was found to be effective in the photochemical reaction, and this could not possibly have brought about dissociation.

**The Ozonisation of Oxygen.** The ozonisation of oxygen by radiation of 2070 Å has been examined by Warburg (1921), who found an efficiency of two molecules of ozone, *i.e.*, three molecules of oxygen, per quantum of absorbed radiation at pressures not greater than 125 atm. In the vicinity of the photochemically active wavelength oxygen shows discontinuous absorption, implying that the primary reaction with the quantum of radiation must be the formation of an excited molecule, thus

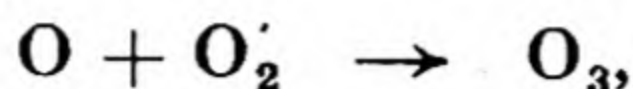




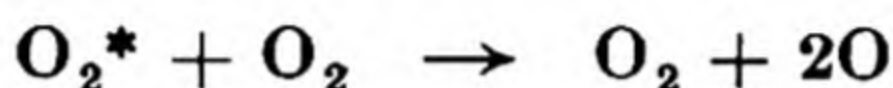
this is followed by the secondary reactions



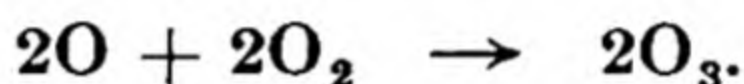
and then



so that two molecules of ozone are formed per quantum of absorbed radiation; the latter of these secondary reactions incidentally must involve a three-body collision or must occur at the walls of the vessel. The quantum of radiation for a wavelength of 2070 Å corresponds to an energy of 128,000 cal. per gm. mol., which is also sufficient to permit the reaction



to occur as the result of a collision; this would be followed by

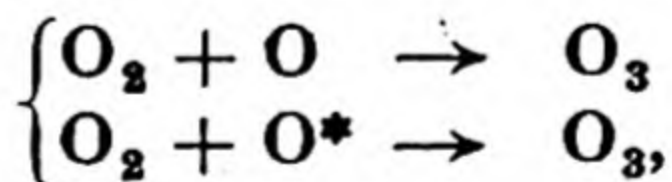


At 2530 Å the energy of the quantum, *i.e.*, 112,000 cal. per gm. mol., does not allow the decomposition into atoms to occur on collision, and in fact at this wavelength the quantum yield is slightly lower than for the 2070 Å radiation.

Vaughan and Noyes (1930) have found that in the ozonisation of oxygen with light of 1700 Å wavelength the photochemical efficiency is also two molecules of ozone per quantum of absorbed radiation. In this spectral region, beyond the convergence limit of the Schumann bands of oxygen, there is continuous absorption indicating that the photochemical reaction is

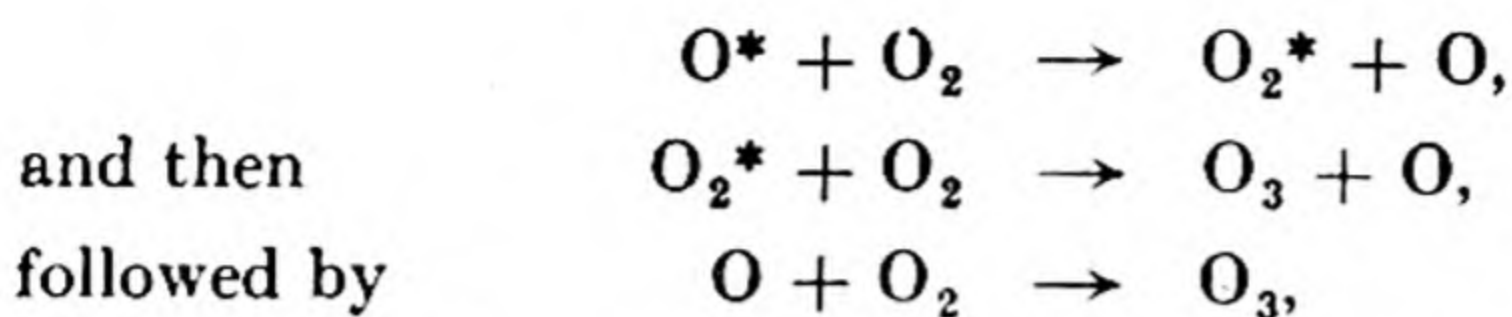


followed by a secondary reaction



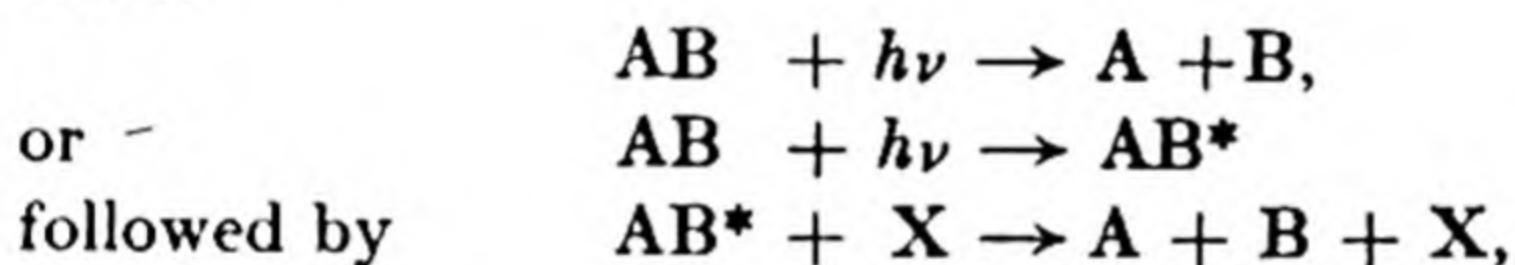
resulting in a quantum efficiency of three, as found experimentally. The secondary processes must involve three-body collisions, or wall reactions, since the energy evolved is so considerable, even though the excited oxygen atom may lose its additional energy before impact with an oxygen molecule. If the energy of the excited oxygen atom were large enough, it might activate an oxygen molecule as the result of a collision, and the latter might then react with another oxygen molecule, thus





as in the reaction at longer wavelengths studied by Warburg. The quantum efficiency of the whole process would then be greater than the experimental value of three; activation of an oxygen molecule in this manner, therefore, does not occur. In any case it is doubtful if the excess energy of the excited oxygen atom is sufficient to raise the oxygen molecule to the requisite energy level.

Other cases are known in which there is no appreciable change in the quantum efficiency as the light passes from a region of continuous absorption, or of pre-dissociation, to one showing rotational and vibrational structure, *e.g.*, the hydrogen-chlorine and hydrogen-bromine reactions, and the decomposition of formaldehyde vapour. The primary stage in each case must be either



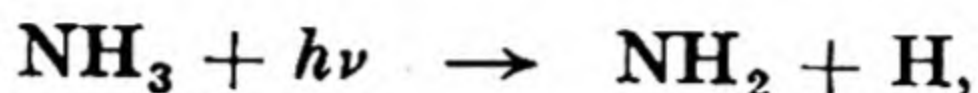
where X may be another molecule of AB or of any other substance which permits the excited AB\* molecule to decompose on collision. The subsequent stages of the process, which are really "dark" reactions, are the same in each case, and so are independent of the primary photochemical stage.

**The Decomposition of Ammonia.** It is generally accepted that electronic bands with definite vibrational lines but diffuse rotational structure are due to a dissociation resulting from an internal energy change (p. 230); such dissociation should not involve collision with any other molecule, and so the quantum efficiency should be at least unity. The band spectrum of ammonia gas is known to be diffuse in the region of 2200 Å to 1600 Å, and radiation of this type is effective in producing photochemical decomposition even at pressures as low as 0.001 mm. of mercury (Bonhoeffer and Farkas, 1928); this indicates that decomposition is independent of collisions, and hence it is somewhat surprising to find quantum yields of less than unity. With radiation of 2000 Å



to 2144 Å the efficiency increases from about 0.15 at ordinary temperatures to 0.5 at 400° C. (Ogg, Leighton and Bergstrom, 1934): increase of pressure at first increases the efficiency and then decreases it.

The primary decomposition process is probably



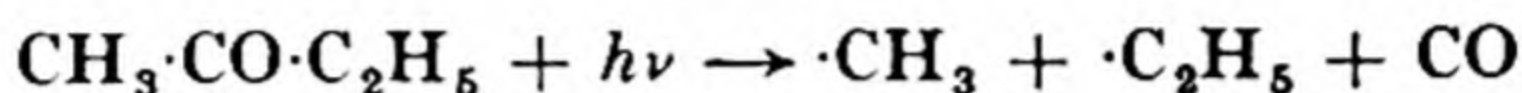
and the poorness of the quantum efficiency must be attributed to recombination of the reaction products. Evidence for this view is provided by the observation that hydrogen atoms, produced by excited mercury atoms, retard the photochemical decomposition of ammonia (Melville, 1932).

An interesting contribution to this subject is provided by the work of Taylor and Jungers (1934): a mixture of ammonia and deuterium, with a little mercury vapour, was exposed to radiations containing the wavelengths of 2100 Å and 2537 Å, and all three deuterio-ammonias,  $\text{NH}_2\text{D}$ ,  $\text{NHD}_2$  and  $\text{ND}_3$ , were detected amongst the products. When the 2100 Å radiation was reduced the amounts of these substances were also decreased. Since this radiation decomposes ammonia, whereas the 2537 Å light dissociates the deuterium, it appears that the two consecutive reactions are:  $\text{NH}_3 + h\nu \rightarrow \text{NH}_2 + \text{H}$ , and  $\text{NH}_2 + \text{D} \rightarrow \text{NH}_2\text{D}$ , since there are more deuterium than hydrogen atoms present in the gas.

**Photolysis of Aldehydes and Ketones.** Aldehydes and ketones in general have a region of continuous absorption in the region 2000 to 3000 Å, which is undoubtedly characteristic of the  $>\text{C}=\text{O}$  group, and light in this wavelength range is able to bring about photochemical decomposition; it is a remarkable fact, however, that there is no breaking of the carbon-oxygen linkage, for no oxygen has been detected amongst the products and the nature of the latter corresponds clearly to the breaking of a carbon-carbon bond. With acetone, for example, the gaseous products of decomposition consist of nearly 50 per cent. of carbon monoxide and the remainder is mainly ethane (Damon and Daniels, 1933; Norrish *et al.*, 1934). In general, two types of photolysis have been observed with aldehydes and ketones.

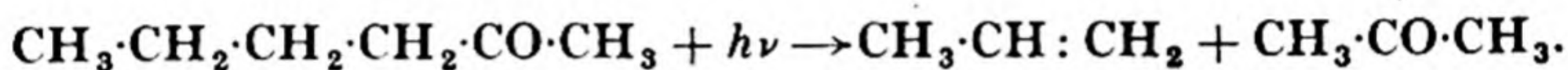


(1) When only short hydrocarbon chains are attached to the carbonyl group, *e.g.*, acetaldehyde, acetone and methyl ethyl ketone, the products are such as to indicate that the linkage broken in the photo-decomposition is that which attaches the alkyl group to the carbonyl carbon atom; thus,



followed by  $\cdot\text{CH}_3 + \cdot\text{C}_2\text{H}_5 \rightarrow \frac{1}{3}(\text{C}_2\text{H}_6 + \text{C}_3\text{H}_8 + \text{C}_4\text{H}_{10})$ .

(2) On the other hand, if the hydrocarbon-chains are relatively long a process occurs in which the chain is broken between the  $\alpha$  and  $\beta$  carbon atoms: thus, methyl butyl ketone decomposes almost entirely into acetone and propylene.



Similar results have been obtained with other ketones and aldehydes (Norrish *et al.*, 1934, 1935; see "Recent Advances in General Chemistry," Chapter IX.).

According to the suggestions of Norrish, the absorption of radiation by the carbonyl group in the first type of photolysis is followed by a switch, of the nature of pre-dissociation, whereby the energy passes from the carbonyl group to the carbon-carbon link *via* the common carbon atom. It may be supposed that at the same time the  $>\text{C}=\text{O}$  passes from the  $^3\Pi$  state, corresponding to carbon in the  $^5S$  state, to the normal  $^1\Sigma$  form, and then ample energy becomes available for the breaking of the two carbon-carbon bonds and the formation of two free radicals which subsequently unite to form hydrocarbons. The fact that the energy switch may not be complete, and some energy may be taken up by other degrees of freedom, probably accounts for the relatively small quantum efficiency, namely about 0.4 for acetone with radiation of 2500 Å to 2900 Å. The second type of photo-decomposition is not so easy to account for: there is no clear indication as to the nature of the process by which the energy absorbed at one part of the molecule, *i.e.*, at the carbonyl group, is transferred almost completely across one carbon-carbon linkage to the next, *i.e.*, the  $\alpha\beta$  bond, which is actually broken. The fact

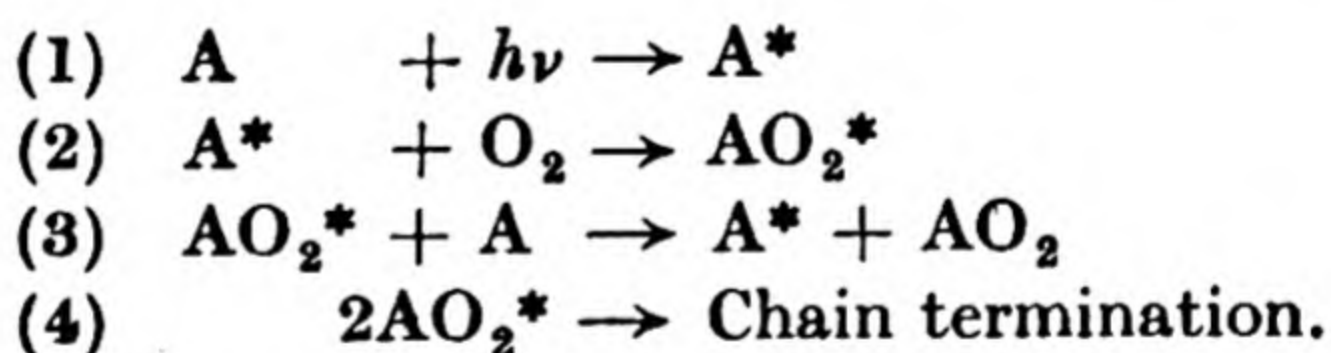


remains, however, that such an energy transfer is possible in relatively complex molecules and this is a result of great importance.

## REACTION KINETICS

By combining the conclusions reached from a study of the band spectra of the reactants and the Einstein law of photochemical equivalence with an examination of the dependence of the velocity of the reaction on the amount of light absorbed and the concentration of the reactants, it is often possible to obtain a great deal of information concerning the mechanism of the process occurring. In order to illustrate the application of the method, which is of particular value when chain reactions are concerned, a simple case will be taken first and more complicated examples will be discussed later.

**Oxidation of Acetaldehyde.** Bowen and Tietz (1930) in a study of the photochemical reaction of gaseous acetaldehyde with oxygen found the rate to be proportional to the square root of the light absorbed and directly proportional to the concentration of aldehyde, but independent of the oxygen concentration. To account for these observations the following chain mechanism was proposed, A representing the aldehyde and  $\text{AO}_2$  the oxidation product:—



Reactions (2) and (3) by repetition produce the chains which are broken by reaction (4). This mechanism is in harmony with the kinetics of the reaction, as may be seen from the following considerations. If  $L$  is the rate of light absorption, expressed in appropriate units, and  $k_2$ ,  $k_3$  and  $k_4$  represent the velocity constants of the corresponding reactions, then it is possible to write

$$d[\text{A}^*]/dt = L + k_3[\text{AO}_2^*][\text{A}]$$

and 
$$-d[\text{A}^*]/dt = k_2[\text{A}^*][\text{O}_2],$$

since  $\text{A}^*$  is formed in processes (1) and (3), and removed in pro-



cess (2). (It should be noted that  $L$  represents the rate of formation of active molecules  $A^*$  in process (1); this is, of course, proportional to the rate of light absorption and so is sometimes written  $k_1 I_{\text{abs}}$  or as  $I_{\text{abs}}$ . It is also proportional to  $I_0[A]$ , where  $I_0$  is the incident light intensity and  $[A]$  the concentration of absorbing molecules; these three forms all appear in the literature.) At any instant the concentration of  $A^*$  will be small and soon after the reaction commences it is reasonable to suppose that a photochemical "stationary state" is attained in which the rate of formation of  $A^*$  is equal to its rate of removal by reaction; if this is so then the *net* rate of change of  $A^*$  with time is zero, and hence

$$d[A^*]/dt = 0 = L + k_3[AO_2^*][A] - k_2[A^*][O_2].$$

Similarly for  $AO_2^*$  in the photostationary state

$$d[AO_2^*]/dt = 0 = k_2[A^*][O_2] - k_3[AO_2^*][A] - k_4[AO_2^*]^2.$$

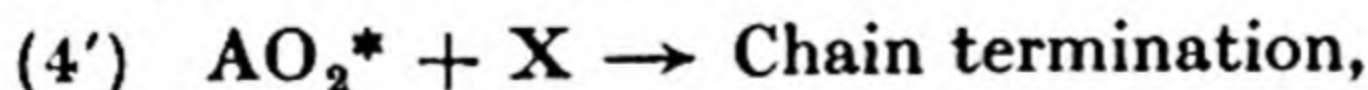
Combining these two equations it follows that

$$L = k_4[AO_2^*]^2.$$

Now the rate of the photochemical reaction is determined by reaction (3) yielding the product  $AO_2$ , and so

$$\begin{aligned} d[AO_2]/dt &= k_3[AO_2^*][A] \\ &= k_3\sqrt{L/k_4}[A] \\ &= k\sqrt{L}[A]; \end{aligned}$$

this is the relationship determined experimentally. It would no doubt be possible to devise other mechanisms leading eventually to the same final equation, but the one presented here is simple and does not involve any improbable assumptions. Further, it accounts for the fact that in the presence of certain inhibitors, *e.g.*, alcohol, the oxidation of acetaldehyde in hexane solution becomes *directly* proportional to the light intensity. The chain breaking reaction (4) is now replaced by



where  $X$  represents the inhibitor, so that in the photostationary state

$$d[AO_2^*]/dt = 0 = k_2[A^*][O_2] - k_3[AO_2^*][A] - k_4'[AO_2^*][X],$$



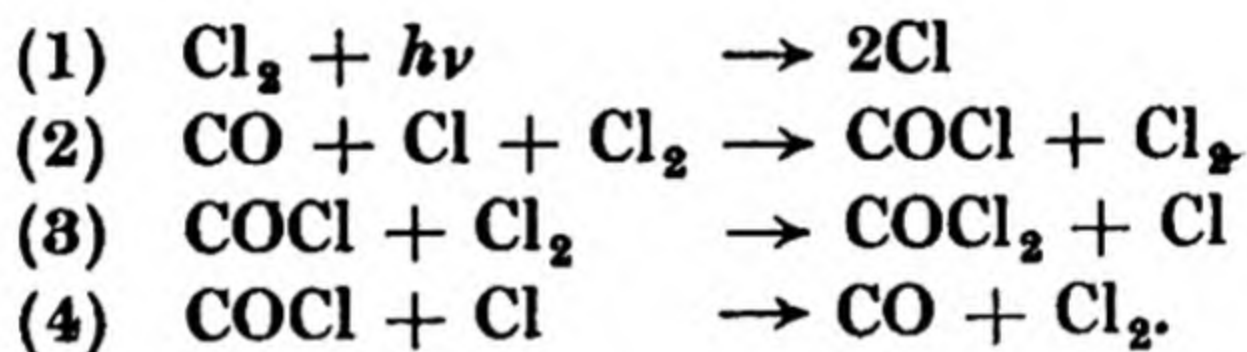
and finally  $d[\text{AO}_2]/dt = k'L[\text{A}][\text{X}]$ .

The square root relationship has given place to one of direct proportionality.

**Carbon Monoxide–Chlorine Reaction.** In some reactions it seems necessary, in order to account for the observed kinetics, to postulate the existence of an intermediate molecule which is not ordinarily stable; the photochemical formation of phosgene provides an example of this type of mechanism. The combination of carbon monoxide and chlorine is a chain reaction, approximately  $1 - 3 \times 10^3$  molecules of chlorine reacting per quantum of light absorbed, in which the rate is given by the equation (Bodenstein *et al.*, 1927 *et seq.*)

$$d[\text{COCl}_2]/dt = k\sqrt{L[\text{CO}]}[\text{Cl}_2].$$

The following mechanism for the chain has been proposed by Lenher and Rollefson (1930), the first step being the dissociation of the chlorine by the light which is in the region of continuous absorption :



The molecule of chlorine in stage (2) acts merely as a third-body (see p. 285) in order to remove the energy developed in the reaction. Assuming that COCl and Cl react very rapidly so that their amount at any instant is small and that each attains a stationary concentration, it follows that

$$d[\text{Cl}]/dt = 0 = 2L + k_3[\text{COCl}][\text{Cl}_2] - k_2[\text{CO}][\text{Cl}][\text{Cl}_2] - k_4[\text{COCl}][\text{Cl}],$$

$$\text{and } d[\text{COCl}]/dt = 0 =$$

$$k_2[\text{CO}][\text{Cl}][\text{Cl}_2] - k_3[\text{COCl}][\text{Cl}_2] - k_4[\text{COCl}][\text{Cl}].$$

A comparison of reactions (3) and (4) shows that the former, involving chlorine molecules, will occur much more rapidly than the latter, since the chlorine atom concentration at any instant is very small; it is thus possible to neglect  $k_4[\text{COCl}][\text{Cl}]$  in com-



parison with  $k_3[\text{COCl}][\text{Cl}_2]$ , and so it follows from the last equation that

$$[\text{COCl}] = [\text{CO}][\text{Cl}]k_2/k_3.$$

Substituting this value in the equation for  $d[\text{Cl}]/dt$  it is found that

$$[\text{Cl}] = \sqrt{2k_3L/k_2k_4}[\text{CO}].$$

Introducing this in the expression for  $[\text{COCl}]$ , the result obtained is

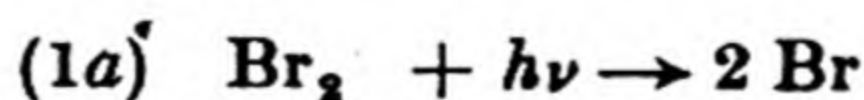
$$[\text{COCl}] = \sqrt{2k_2L[\text{CO}]/k_3k_4}.$$

The rate of formation of phosgene is determined by process (8), that is,

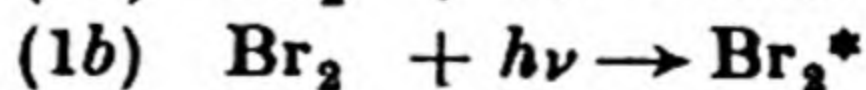
$$\begin{aligned} d[\text{COCl}_2]/dt &= k_3[\text{COCl}][\text{Cl}_2] \\ &= \sqrt{2k_2k_3L[\text{CO}]/k_4}[\text{Cl}_2] \\ &= k\sqrt{L[\text{CO}]}[\text{Cl}_2]. \end{aligned}$$

Although this equation is in harmony with the observations it does not follow that the mechanism proposed here is correct; it is, however, simple and does not present any obvious flaws and so may be accepted until some reason appears for its abandonment. It may be added that Rollefson (1983) has shown that the molecule  $\text{Cl}_3$ , perhaps in place of  $\text{Cl}_2 + \text{Cl}$ , may play a part in the reaction.

**The Hydrogen-Bromine Reaction.** The photochemical union of moist hydrogen and bromine vapour in visible light is a chain reaction, although the efficiency is less than 0.01 molecules of hydrogen bromide per quantum of radiation absorbed. This reaction presents a number of interesting features and so merits discussion in some detail. The band spectrum of bromine shows continuous absorption at wavelengths less than 5107 Å, but the hydrogen-bromine combination can occur at the same velocity when the reaction is initiated either by light of lower or higher wavelength (Jost, 1929). The primary process can then be either



or



followed by

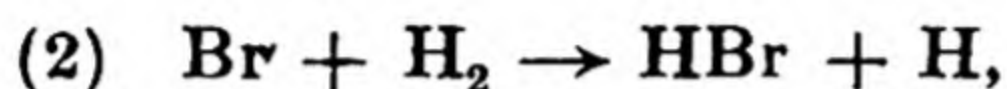




according to the wavelength of the light used. Both these processes lead to the result that

$$d[\text{Br}]/dt = 2L,$$

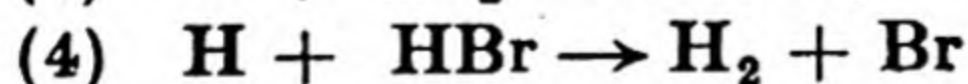
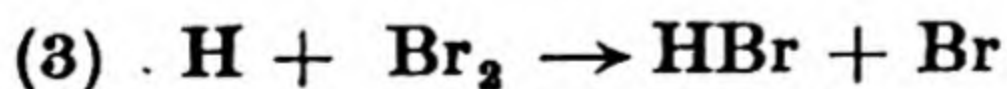
provided every excited molecule  $\text{Br}_2^*$  dissociates before it loses its energy. The subsequent stages and consequently the reaction rate will thus be independent of the wavelength of the incident radiation. The second stage in the reaction must be



but this is an endothermic process involving 17,000 cal. and so will only occur readily when there is a collision between reactants containing a large amount of energy. Such collisions are probably infrequent, and so many of the bromine atoms resulting from the primary dissociation will re-unite; it follows, therefore, that only a small proportion of the quanta of radiation originally absorbed will be effective in producing hydrogen bromide molecules, and so the quantum efficiency is low. This is, however, the only method by which the reaction can proceed under the experimental conditions, and the hydrogen atom produced sets up a reaction chain. The nature of this chain has been elucidated by Bodenstein and Lütkemeyer (1924) as the result of a study of the kinetics of the reaction; it was found that the rate of formation of hydrogen bromide was given by the somewhat complicated relationship

$$\frac{d[\text{HBr}]}{dt} = \frac{k\sqrt{L}[\text{H}_2][\text{Br}_2]}{10[\text{Br}_2] + [\text{HBr}]},$$

and in order to account for it the following stages, subsequent to those already mentioned, were suggested:



The bromine atoms may also be removed by union with hydrogen atoms, but as the concentration of the latter will be very small and the process will, in any case, require a three-body collision the extent of the reaction can be ignored. Considering that photo-



stationary states are attained for bromine and hydrogen atoms, it follows that

$$d[\text{Br}]/dt = 0 =$$

$$2L - k_2[\text{Br}][\text{H}_2] + k_3[\text{H}][\text{Br}_2] + k_4[\text{H}][\text{HBr}] - k_5[\text{Br}]^2$$

$$\text{and } d[\text{H}]/dt = 0 = k_2[\text{Br}][\text{H}_2] - k_3[\text{H}][\text{Br}_2] - k_4[\text{H}][\text{HBr}].$$

Solving for  $[\text{H}]$  and  $[\text{Br}]$  it is found that

$$[\text{Br}] = \sqrt{2L/k_5}$$

$$\text{and } [\text{H}] = (k_2[\text{H}_2]\sqrt{2L/k_5})/(k_3[\text{Br}_2] + k_4[\text{HBr}]).$$

The net rate of formation of hydrogen bromide is

$$d[\text{HBr}]/dt = k_2[\text{Br}][\text{H}_2] + k_3[\text{H}][\text{Br}_2] - k_4[\text{H}][\text{HBr}]$$

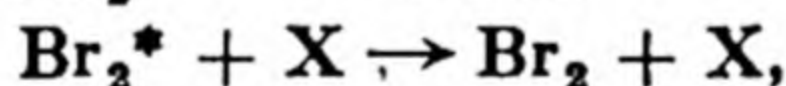
$$= \frac{2k_2k_3\sqrt{2L/k_5}[\text{H}_2][\text{Br}_2]}{k_3[\text{Br}_2] + k_4[\text{HBr}]}$$

$$= \frac{k\sqrt{L}[\text{H}_2][\text{Br}_2]}{k'[\text{Br}_2] + [\text{HBr}]}.$$

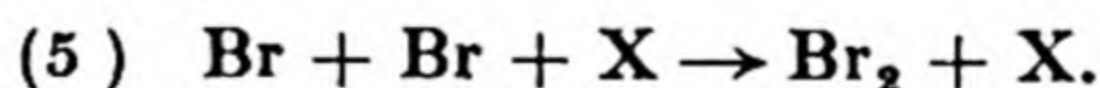
This is exactly the form of the velocity equation found to explain the observations of Bodenstein and Lütkenmeyer. Strictly speaking, this relationship holds only at constant pressure, and Jost (1929) has extended it to apply to various total pressures; he finds that the rate of formation of hydrogen bromide is then inversely proportional to the square root of the gas pressure in addition to the terms already included above. This is accounted for by supposing that stage (5) in the process described is replaced by three stages:



and



the life of the  $\text{Br}_2^*$  being very short. The same result may, however, be obtained by supposing that reaction (5), as might be expected, is a three-body process in the gas phase, provided the pressure is not too high, viz.,



The velocity equation then becomes

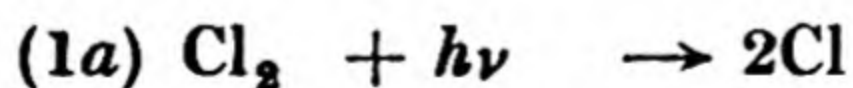
$$\frac{d[\text{HBr}]}{dt} = \frac{k\sqrt{L/[\text{X}]}[\text{H}_2][\text{Br}_2]}{k'[\text{Br}_2] + [\text{HBr}]}$$



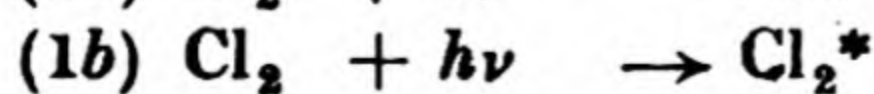
and if any molecular species present can act as a remover of energy in (5') then  $[X]$  is proportional to the total pressure and the resulting equation is of the form deduced by Jost. At low pressures the chain-terminating process (5') should occur mainly at the walls of the reacting vessel, and an inert gas should increase the velocity of the hydrogen-bromine reaction to the extent to which it can prevent access to the walls. The following gases were found to have the expected effect, decreasing in the order given: carbon tetrachloride, carbon dioxide, nitrogen and oxygen, argon, hydrogen and helium. This is also the order of decreasing "collision area" of the molecules named (Ritchie, 1984). At high pressures the process (5') takes place chiefly in the gas phase, and inert gases then decrease the reaction velocity.

**The Hydrogen-Chlorine Reaction.** The combination of hydrogen and chlorine in the presence of light has probably been studied more than any other photochemical reaction, and in spite of many investigations carried out over a period of about eighty years the problems it presents are far from being solved. As will be seen shortly, the hydrogen-chlorine reaction differs in many respects from the corresponding hydrogen-bromine reaction already discussed. The band spectrum of chlorine has a convergence limit at 4785 Å, and until recently it was not certain whether light of longer wavelength was effective in the photochemical reaction; the work of Allmand (1980, *et seq.*) and of Hertel (1981) has now definitely established that the union of hydrogen and chlorine may be brought about by light of 5461 Å, which is apparently unable to dissociate the chlorine into atoms. The quantum efficiency, which is practically constant in the region of continuous absorption, commences to fall off at 4900 Å, and is less than one-third of this value at 5461 Å.

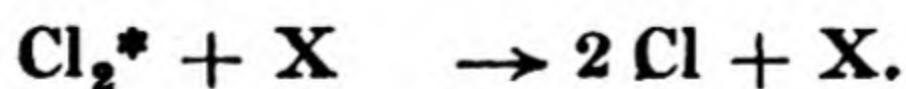
The first stage of the combination must evidently be either



or



followed by

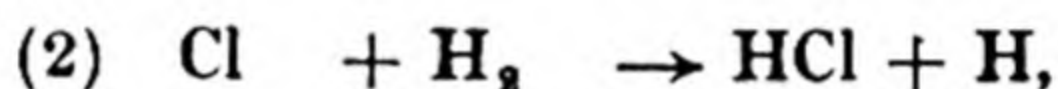


according as the radiation is in the continuous or the banded region.



Craggs and Allmand (1936), however, consider it more probable that all the atoms result by process (1a) and not by (1b). The 5461 Å radiation is equivalent to 52,000 cal. per gm. mol., but about 56,800 cal. are required to dissociate 1 gm. mol. of chlorine into normal atoms. From a consideration of the vibrational energy of the chlorine molecule it is evident that the 5461 Å radiation would be sufficient to bring about dissociation of molecules for which the vibrational quantum number is 8 or 4, and normal chlorine gas will contain a fair proportion of such molecules. There is reason to believe that although the 5461 Å line appears in the banded region of the spectrum, there is a continuous background corresponding to a super-imposed pre-dissociation process, in which molecules in the higher vibrational levels can take part.

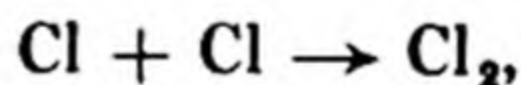
After the formation of chlorine atoms, whatever the mechanism, the next stage is



and this is an exothermic process which takes place very readily ; as it is probably followed by



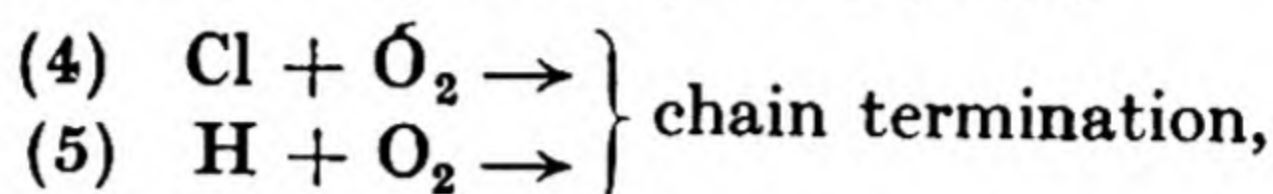
a chain reaction occurs with a very high quantum efficiency (see p. 304). When Nernst originally suggested the atom chain mechanism for the hydrogen-chlorine reaction he considered that chains were broken by the union of chlorine atoms, thus



and if this were the case the rate of reaction, as in the combination of hydrogen and bromine in which chains terminate by the union of bromine atoms, should be proportional to the square root of the light intensity. This mechanism for the breaking of chains may be operative if specially purified chlorine, free from oxygen, is used and no other method is available for removing the chlorine atoms ; the reaction rate under these conditions apparently depends on the square root of the light absorbed (Chapman and Gibbs, 1931). In the great majority of investigations the rate of union of hydrogen and chlorine has been found to be directly



proportional to the light intensity, and this is attributed to the action of oxygen, which can only be removed from chlorine with great difficulty, as being the effective means of terminating reaction chains. Two processes probably occur, viz.,



in addition to the union of chlorine atoms which may occur to a small extent, especially at the walls of the vessel. Bodenstein (1932) has considered the consequences of regarding (5) as the chief chain terminating process; thus at the stationary state for hydrogen and chlorine atoms,

$$d[\text{Cl}]/dt = 0 = 2L - k_2[\text{Cl}][\text{H}_2] + k_3[\text{H}][\text{Cl}_2]$$

$$\text{and } d[\text{H}]/dt = 0 = k_2[\text{Cl}][\text{H}_2] - k_3[\text{H}][\text{Cl}_2] - k_5[\text{H}][\text{O}_2].$$

From the second of these equations it follows that

$$[\text{H}] = 2L/k_5[\text{O}_2],$$

and from the first

$$[\text{Cl}] = (2L + k_3[\text{H}][\text{Cl}_2])/k_2[\text{H}_2].$$

If a long chain is produced, as is evidently the case, the term  $2L$ , representing the rate of production of chlorine atoms in the primary process, may be neglected in comparison with  $k_3[\text{H}][\text{Cl}_2]$  which is the rate of formation of a large proportion of the hydrogen chloride, and so

$$\begin{aligned} [\text{Cl}] &\approx k_3[\text{H}][\text{Cl}_2]/k_2[\text{H}_2] \\ &\approx 2k_3L[\text{Cl}_2]/k_2k_5[\text{H}_2][\text{O}_2]. \end{aligned}$$

The net rate of the photochemical reaction is given by

$$\begin{aligned} d[\text{HCl}]/dt &= k_2[\text{Cl}][\text{H}_2] + k_3[\text{H}][\text{Cl}_2] \\ &= 4k_3L[\text{Cl}_2]/k_4[\text{O}_2] \\ &= kL[\text{Cl}_2]/[\text{O}_2]. \end{aligned}$$

This is the equation found by Bodenstein and Dux (1913) to be applicable under certain conditions for mixtures containing a small quantity of oxygen, provided the hydrogen and chlorine were present in almost equivalent amounts. If both reactions (4) and (5) are able to end the reaction chains then it can be shown (Bodenstein, 1931) that the rate of reaction should be given by



$$\frac{d[\text{HCl}]}{dt} = \frac{4 k_2 k_3 L [\text{H}_2] [\text{Cl}_2]}{[\text{O}_2](k_2 k_4 [\text{H}_2] + k_3 k_5 [\text{Cl}_2])}$$

which is of the form found by Thon (1926) to be in general agreement with many experimental observations.

In spite of the deduction of these equations the mechanism discussed here may not be correct, as it does not account for many of the confusing phenomena observed in the photochemical union of hydrogen and chlorine. Until recently it was believed that a definite, although small, concentration of water vapour was essential to the reaction and various mechanisms were proposed with a molecule of water taking part in process (2); the work of Allmand and Craggs (1932), of Bodenstein and Bernreuther (1933), and of Rollefson and Potts (1933) shows, however, that the photochemical reaction occurs even with the dried gases. Rodebush and Klingelhofer (1933) have also found that water has no influence on the chain reaction between hydrogen and chlorine initiated by the introduction of chlorine atoms. It is interesting to observe that two of the stages in the mechanism involving a water molecule, proposed by Bodenstein (1931), have been shown to be highly improbable by calculations based on wave mechanics.

It has been possible here to touch only very briefly and in outline on the hydrogen-chlorine reaction, and there are many investigations to which no reference has been made. In several instances the conclusions drawn by different workers are contradictory, and further observations under rigidly controlled conditions will be necessary before many of the points in doubt can be cleared up.

## REFERENCES

- ALLMAND *et al.* *J. Chem. Soc.*, 1930, 2709; 1934, 157; 1936, 241; *Ann. Reports*, 1925, 22, 333\*; *Trans. Faraday Soc.*, 1926, 21, 438\*; Discussion on the Critical Increment of Homogeneous Reactions, *Chem. Soc.*, 1931, p. 22.  
 ALYEA. *J. Amer. Chem. Soc.*, 1930, 52, 2743.  
 ALYEA and BÄCKSTRÖM. *Ibid.*, 1929, 51, 90.  
 ALYEA and LIND. *Ibid.*, 1930, 52, 1853.  
 BATES and TAYLOR. *Ibid.*, 1928, 50, 771.  
 BLACET *et al.* *Ibid.*, 1932, 54, 3165; 1933, 55, 1766; 1936, 58, 278.



- BODENSTEIN *et al.* *Z. physikal. Chem.*, 1924, 114, 208 ; 1926, 119, 123 ; 1929, B3, 459 ; *Trans. Faraday Soc.*, 1926, 21, 525 ; 1931, 27, 409, 413 ; *Z. Elektrochem.*, 1932, 38, 911.
- BOWEN *et al.* *Trans. Faraday Soc.*, 1926, 21, 543 ; *J. Chem. Soc.*, 1926, 129, 1607 ; 1930, 234 ; 1932, 1200 ; Discussion on the Critical Increment of Homogeneous Reactions, *Chem. Soc.*, 1931, p. 15 ; *Ann Reports*, 1933, 30, 46\*.
- CHAPMAN. *Trans. Faraday Soc.*, 1926, 21, 547.
- CHAPMAN and GIBBS. *Nature*, 1931, 127, 854.
- CREMER. *Z. physikal. Chem.*, 1927, 128, 285.
- DICKINSON and BAXTER. *J. Amer. Chem. Soc.*, 1928, 50, 774.
- Discussion on Free Radicles. *Trans. Faraday Soc.*, 1934, 30, 3-248\*.
- Discussion on Photochemical Processes. *Ibid.*, 1931, 27, 359-572\*.
- Discussion on Photochemical Reactions in Liquids and Gases. *Ibid.*, 1926, 21, 438-658\*.
- EINSTEIN. *Ann. Physik*, 1912, 37, 832 ; 38, 881 ; *J. Physique*, 1913, 3, 277 ; *Verh. d. deut. Phys. Ges.*, 1916, 18, 318.
- FRANCK. *Trans. Faraday Soc.*, 1926, 21, 536.
- GERKE. *J. Amer. Chem. Soc.*, 1927, 49, 2071.
- GRIFFITH and McKEOWN. "Photo-processes in Gaseous and Liquid Systems," 1929\*.
- HENRI and WURMSER. *J. Phys. Radium*, 1927, 8, 289.
- HERTEL. *Z. physikal. Chem.*, 1931, B14, 443.
- JOST. *Ibid.*, 1929, B3, 95.
- KIMBALL and EYRING. *J. Amer. Chem. Soc.*, 1932, 54, 3876.
- KISTIAKOWSKY. *Ibid.*, 1927, 49, 2194 ; 1930, 52, 102 ; "Photochemical Processes," 1928\*.
- KORNFELD and STEINER. *Z. Physik*, 1927, 45, 325.
- LENHER and ROLLEFSON. *J. Amer. Chem. Soc.*, 1930, 52, 500.
- LEWIS. *Proc. Nat. Acad. Sci.*, 1927, 13, 720.
- LIND and LIVINGSTON. *J. Amer. Chem. Soc.*, 1930, 52, 593.
- MECKE. *Physikal. Z.*, 1932, 33, 1 ; *Trans. Faraday Soc.*, 1931, 27, 359
- MELVILLE. *Ibid.*, 1932, 28, 885 ; *Proc. Roy. Soc.*, 1932, 138A, 384.
- NORRISH *et al.* *J. Chem. Soc.*, 1927, 761 ; 1929, 1158, 1604, 1611 ; 1932, 1518 ; 1933, 1533 ; 1934, 874, 1456 ; 1935, 455, 1504, 1638 ; *Proc. Roy. Soc.*, 1933, 140A, 99, 112, 713.
- OGG, LEIGHTON and BERGSTROM. *J. Amer. Chem. Soc.*, 1934, 56, 318.
- OLDENBERG. *Z. Physik*, 1923, 18, 1.
- RITCHIE. *Proc. Roy. Soc.*, 1934, 146A, 828.
- RODEBUSH and KLINGELHOEFER. *J. Amer. Chem. Soc.*, 1933, 55, 130.
- ROLLEFSON *et al.* *Ibid.*, 1931, 53, 1728 ; 1933, 55, 142, 148, 860 ; 1934, 56, 579, 1091 ; 1935, 57, 1027.
- STYLE. "Photochemistry," 1930\*.
- TAYLOR *et al.* *Trans. Faraday Soc.*, 1926, 21, 560 ; *J. Physical Chem.*, 1925, 29, 1140 ; 1928, 32, 481\* ; 1930, 34, 2049\* ; *J. Chem. Physics*, 1934, 2, 452.
- VAUGHAN and NOYES. *J. Amer. Chem. Soc.*, 1930, 52, 559.
- WARBURG. *Z. Elektrochem.*, 1920, 26, 54 ; 1921, 27, 133.
- WIIG and KISTIAKOWSKY. *J. Amer. Chem. Soc.*, 1932, 54, 1806.

\* Review papers and books, wherein further references are to be found, are marked by an asterisk.



## THE PROPERTIES OF SURFACES

surface of water has in recent years, mainly as a result of the work of Langmuir and of Adam, yielded information concerning molecular dimensions, and has brought to light a number of interesting phenomena in connection with the behaviour of molecules in surfaces.

[illegible]



On the other hand, if  $\gamma_B$  is greater than the sum of  $\gamma_A$  and  $\gamma_{AB}$  the globule will not be stable, but the large value of  $\gamma_B$  will cause the liquid oil A to spread over the surface of B. Suppose the liquid B is water, then  $\gamma_B$  is about 73 dynes per cm. at ordinary temperatures; if A is a long chain aliphatic hydrocarbon then  $\gamma_A$  is about 30 dynes per cm., and the interfacial tension  $\gamma_{AB}$  approximately 57 dynes. In this case  $\gamma_A + \gamma_{AB}$  is 87 dynes, and this is greater than  $\gamma_B$  (73 dynes); the hydrocarbon oil will thus not spread on water but will form a stable globule. On the other hand, if A is a long chain fatty acid, *e.g.*, oleic acid, for which  $\gamma_A$  is 32, and  $\gamma_{AB}$  (oleic acid-water) is 16 dynes, then  $\gamma_A + \gamma_{AB}$  is 48 dynes; this value is considerably less than the surface tension of water, and so oleic acid should, and does, spread readily on the surface of water. In general the difference between  $\gamma_A + \gamma_{AB}$  and  $\gamma_B$  is a measure of the spreading tendency of B on A, and is called the "spreading coefficient." It must be emphasised that if A and B are soluble in one another to any appreciable extent the values of  $\gamma_A$  and  $\gamma_B$  to be used in determining the tendency to spread are those for A and B, respectively, saturated with the other liquid.

**Dupré's Equation.** Consider a layer of liquid A on the surface of another liquid B, and suppose the area of contact between B and A is reduced by 1 sq. cm. ; at the same time the individual areas of the surfaces of A and B must each be increased by 1 sq. cm. Since the work done in producing any surface is equal to the surface tension multiplied by the area of the surface formed, the work done in increasing the surfaces of A and B is  $\gamma_A + \gamma_B$ , and the work resulting from the diminution of the AB interface is  $\gamma_{AB}$ . The net work done is thus  $\gamma_A + \gamma_B - \gamma_{AB}$  ergs, and this must equal the work done against the forces of adhesion acting across the interface between the liquids A and B, since no other energy changes are involved in the process under consideration. Hence it is possible to write

$$\gamma_A + \gamma_B - \gamma_{AB} = W_a \quad . \quad . \quad . \quad . \quad . \quad . \quad (ii.)$$

where  $W_a$  is the "adhesional work" between A and B; this relationship is known as Dupré's equation, and was first deduced in 1869. If a single liquid, for example A, is imagined to be in the



form of a column of 1 sq. cm. cross section, and the two ends of the column are pulled so that the liquid is divided into two parts without any lateral contraction, then two new surfaces each of 1 sq. cm. area will be formed. The work required to form these two surfaces is  $2\gamma_A$ , and this must be done against the forces of cohesion of the liquid A; the quantity  $2\gamma_A$  ergs is thus sometimes referred to as the "cohesional work." For the liquid A to spread on B it is required, as already seen, that

$$\gamma_B > \gamma_A + \gamma_{AB}; \quad \dots \dots \dots (ia.)$$

hence it is necessary that

$$\gamma_B - \gamma_A - \gamma_{AB} > 0 \quad \dots \dots \dots (iii.)$$

Adding  $2\gamma_A$  to each side it follows that for spreading

$$\gamma_A + \gamma_B - \gamma_{AB} > 2\gamma_A \quad \dots \dots \dots (iv.)$$

The left-hand side of this expression is equal to the adhesional work between A and B ( $W_a$ ); hence for spreading

$$W_a > 2\gamma_A \quad \dots \dots \dots (v.)$$

In other words, for the liquid A to spread on B it is necessary that the force of adhesion between A and B shall be greater than the force of cohesion ( $2\gamma_A$ ) of A itself; that is, the attraction between the molecules of A and B must be larger than the attractions between the A molecules themselves. This conclusion appears to be in agreement with what might have been expected from first principles, and gives a simple physical interpretation of the spreading of oil films. If the cohesional force in a liquid A is greater than the force of adhesion between A and B, then it is clear that the molecules of A will tend to cohere rather than to spread on the surface of B; in this case, as is to be anticipated, a globule of oil will form.

**Polar Groups and Spreading.** In the course of a very extensive study of surface and interfacial tensions, Harkins (1917) observed that almost all the substances for which the determinations indicated spreading would occur on the surface of water had one factor in common; they all contained in the molecule a "polar" group (see Chapter III.), such as  $-\text{OH}$ ,  $-\text{COOH}$ ,  $-\text{CHO}$ ,  $-\text{CN}$ ,  $-\text{NH}_2$  or  $-\text{CONH}_2$ . Now it is well known that the



presence of one of these strongly polar groups generally confers solubility in water on the molecules to which it is attached; for example, although methane and ethane are sparingly soluble, the corresponding alcohols are miscible with water in all proportions. As the length of the hydrocarbon-chain is increased, however, the solubility of the alcohol decreases very markedly. This decrease is probably not due to any diminution in the attraction between the water and the — OH group, which is the primary cause of the solubility, since the adhesional force between an alcohol and water is almost independent of the length of the hydrocarbon-chain, as shown by the results in Table LX.

TABLE LX.—*Adhesional Work at Water-Alcohol Interfaces*

Alcohol					$W_a$ (ergs)
Methyl	$\text{CH}_3\text{OH}$	.	.	.	95.5
Ethyl	$\text{C}_2\text{H}_5\text{OH}$	.	.	.	95.2
Propyl	$\text{C}_3\text{H}_7\text{OH}$	.	.	.	96.5
Butyl	$\text{C}_4\text{H}_9\text{OH}$	.	.	.	97.3
Octyl	$\text{C}_8\text{H}_{17}\text{OH}$	.	.	.	91.8

**The Orientation of Long Chain Molecules.** The low solubility of the higher alcohols, therefore, appears to be due to the fact that the long chain is difficult to pull into the water, and when the alcohol forms a film on the surface of water the hydrocarbon-chains will presumably be oriented away from the water. The small attraction between a hydrocarbon-chain and water, as already mentioned, is insufficient to cause a simple hydrocarbon oil to spread on the surface of water. Since the addition of an — OH group to the end of a hydrocarbon-chain increases the attraction of the molecules for water, spreading can occur. This attraction, as measured by the force of adhesion, is almost independent of the length of the chain (Table LX.), and so it seems very probable that the — OH group is oriented towards the water in every case. According to these views any molecule with a polar group will tend to dissolve in water, but if it has a long hydrocarbon-chain dissolution is prevented; the attraction between the polar group and the water molecules, however, causes the substance to spread



on water, whereas the original hydrocarbon does not spread in this manner. In the surface film formed by the organic compound the polar group is oriented towards, and possibly dissolved in, the water, whereas the hydrocarbon-chain points away, and is out of the water surface. It is thus possible to obtain a chemical, as well as a physical, interpretation of the spreading of oils on water.

**Unimolecular Films.** If a very small quantity of an insoluble spreading oil—only just enough to form a layer one molecule in thickness—is put on to the surface of water, then it may be supposed that the molecules of oil arrange themselves with their polar groups all attached to the water surface, and the hydrocarbon-chains arranged parallel to one another, more or less vertically, above the polar groups (see Fig. 29). When the film of oil is complete, and the molecules are packed together as closely as possible, the upper exposed surface of the system will consist entirely of methyl, or similar, groups forming the ends of the hydrocarbon-chains opposite to those at which the polar groups are attached. If a further quantity of oil is now added to the surface there is no tendency for these molecules to become “anchored” to the water surface, as the latter is entirely covered by an oil film; hence there will be no influence tending to encourage the formation of a second molecular layer. In fact the polar groups of the molecules will tend to associate together, and this can occur more readily if the oil forms globules rather than if it is spread out in a film. It may be expected, therefore, that if an oil, such as oleic acid, is added gradually to clean water the molecules will spread evenly on the surface until a complete unimolecular layer is formed; further addition of oil, however, should result in the formation of a number of small clusters, or droplets, many molecules in thickness.

### THE GIBBS ADSORPTION EQUATION

An interesting confirmation of the view that a surface film consists of closely packed oriented molecules was obtained by Langmuir (1917) from a study of the Gibbs adsorption equation. It is well known that if a solute lowers the surface tension of a











$$\frac{\gamma}{\gamma_0} = 1 - B \log \left( \frac{c}{A} + 1 \right) \quad \cdot \cdot \cdot \cdot \cdot \quad (\text{x.})$$

where  $\gamma$  is the surface tension of a solution of concentration  $c$ ,  $\gamma_0$  is that of pure water, and  $A$  and  $B$  are constants. The value of  $B$  was found to be a constant for all the fatty acids examined, but  $A$  decreased with increasing length of the hydrocarbon-chain. For fairly concentrated solutions the integer 1 may be neglected in comparison with  $c/A$ , and the equation, as Langmuir showed, reduces to

$$\frac{\gamma}{\gamma_0} = 1 - B \log \frac{c}{A} \quad \cdot \cdot \cdot \cdot \cdot \quad (\text{xi.})$$

For these solutions  $\gamma$  is a linear function of  $\log c$ , and hence of  $\ln c$ , and the equation is of the same type as that proposed by Milner (1907). This result indicates, as already shown, that for all the fatty acids studied a limiting adsorption is attained as the concentration of the solution is increased. On differentiation equation (xi.) yields

$$\frac{d\gamma}{d \ln c} = - \frac{B\gamma_0}{2.302} \quad \cdot \cdot \cdot \cdot \cdot \quad (\text{xii.})$$

and hence

$$\Gamma_\infty = \frac{B\gamma_0}{2.302 RT} \quad \cdot \cdot \cdot \cdot \cdot \quad (\text{xiii.})$$

Since  $B$  was found to be the same for the various acids it is clear that the limiting number of molecules adsorbed per unit area is independent of the nature of the acid; consequently the area occupied by each molecule is also the same for each of the acids examined, irrespective of the length of the hydrocarbon-chain. This conclusion is just what would have been expected from the theory that in the surface a single layer is formed of oriented and closely packed molecules. An examination of equation (xi.) shows that the smaller the value of  $A$  the lower is the concentration at which the limiting state of adsorption is reached. It has been already stated that  $A$  decreases with increasing length of chain, and at the same time the solubility of the acid decreases; it appears, therefore, that the less soluble the acid the more readily is the complete unimolecular layer formed. This result suggests that the hydrocarbon-chain, which confers insolubility, arranges



itself more or less perpendicularly to the surface so as to point away from the bulk of the water, whereas the polar group remains in, or just below, the surface ; the longer the chain the greater the tendency for it to come out of the water and so the more readily does the surface film become complete. It is obvious that this view of the structure of the surface requires that when the closely packed single layer of oriented molecules of fatty acid is formed completely, the area occupied by each should be independent of the length of the hydrocarbon-chain, but should depend only on the cross-section, which is presumably constant ; these expectations are in agreement with the experimental results.

**Molecular Dimensions.** The value of  $B$  in equation (x.) is known to be 0.411 from the work of Szyszkowski, and so the area occupied by a single molecule of any of the fatty acids studied is found to be  $31 \times 10^{-16}$  sq. cm. This result, as will be shown later, is in agreement with values for the area of molecules obtained in other ways. The area of cross-section of a hydrocarbon-chain, according to the arguments presented in the previous paragraphs, should thus be  $31 \times 10^{-16}$  sq. cm., and hence the diameter is about  $5 \times 10^{-8}$  cm. ; this value is in general agreement with the order of molecular dimensions.

## SURFACE FILMS

**Tension Measurements.** By means of an interesting series of experiments commenced in 1891 and continued to the present day, further information has been obtained concerning the orientation of molecules in surface films ; incidentally some remarkable phenomena have been observed, and these will be discussed in the sections which follow.

It was discovered by Miss Pockels (1891) that the area covered by a spreading oil on the surface of water could be varied at will by confining the film between movable barriers ; these were made of strips of glass placed right across a tray filled with water on which the oil was spread. Lord Rayleigh (1899) repeated and extended the experiments of Miss Pockels, and confirmed the observation that as the area occupied by a given amount of olive oil on the surface of water was diminished by bringing the barriers



closer together, the surface tension remained almost unchanged until a certain area was reached, when the tension dropped suddenly to about half the original value for water. From the volume of oil placed on the surface and the area it occupies, the thickness of the film at any stage may be calculated; it was found that the sudden fall of surface tension occurred when the thickness of the film was about  $1.0 \times 10^{-7}$  cm. From the similarity of this value with ordinary molecular dimensions Rayleigh concluded that the fall in surface tension occurred when the surface was just covered with a complete layer one molecule in thickness. Further observations of oil films on water were made by Devaux and by Marcelin (1908–1914) and these confirmed the view that the films were unimolecular.

In 1917 a considerable advance in experimental technique was made by Langmuir, and this opened up a new era in the study of surface films. Miss Pockels and Lord Rayleigh had measured the surface tension of the water by determining the force necessary to pull a thin blade out of the surface (Wilhelmy's method), and Devaux and Marcelin studied the films by sprinkling talc on the surface so as to render the extent of the oil visible. In the course of his preliminary investigations Langmuir noted that the forces exerted by the oil films on the paper barriers which enclosed them were quite considerable, and so he conceived the idea of measuring these forces by means of a balance. A shallow trough was filled with water, and near one end was floated a paper strip (*B*) which was just less than the width of the trough; this strip acted as one of the barriers to the oil film being experimented upon. Jets of air (*CC*) were used to prevent leakage of oil through the narrow spaces between the ends of the strip and the sides of the trough. Vertical glass rods attached to the paper strip were fixed to the main knife-edge (*E*) of a balance, so that any movement of the strip caused by a force acting in the liquid surface caused a displacement of the equilibrium of the balance; the weight required to be added to the balance pan (*D*) to bring the paper float back to its original position is a measure of the force acting on the latter (Fig. 25). A definite amount of an oil, insoluble in water, was placed on the surface of the water in the trough by dropping



on to it a suitable volume of a solution of the oil in benzene at a known concentration; the benzene soon evaporated, leaving a clean oil film. Another paper barrier (*A*), which went right across the width of the trough, and so could not float, was placed at the other end of the trough; by moving this barrier towards the floating one the area covered by the oil could be varied at will, and the force exerted for different areas could be determined by

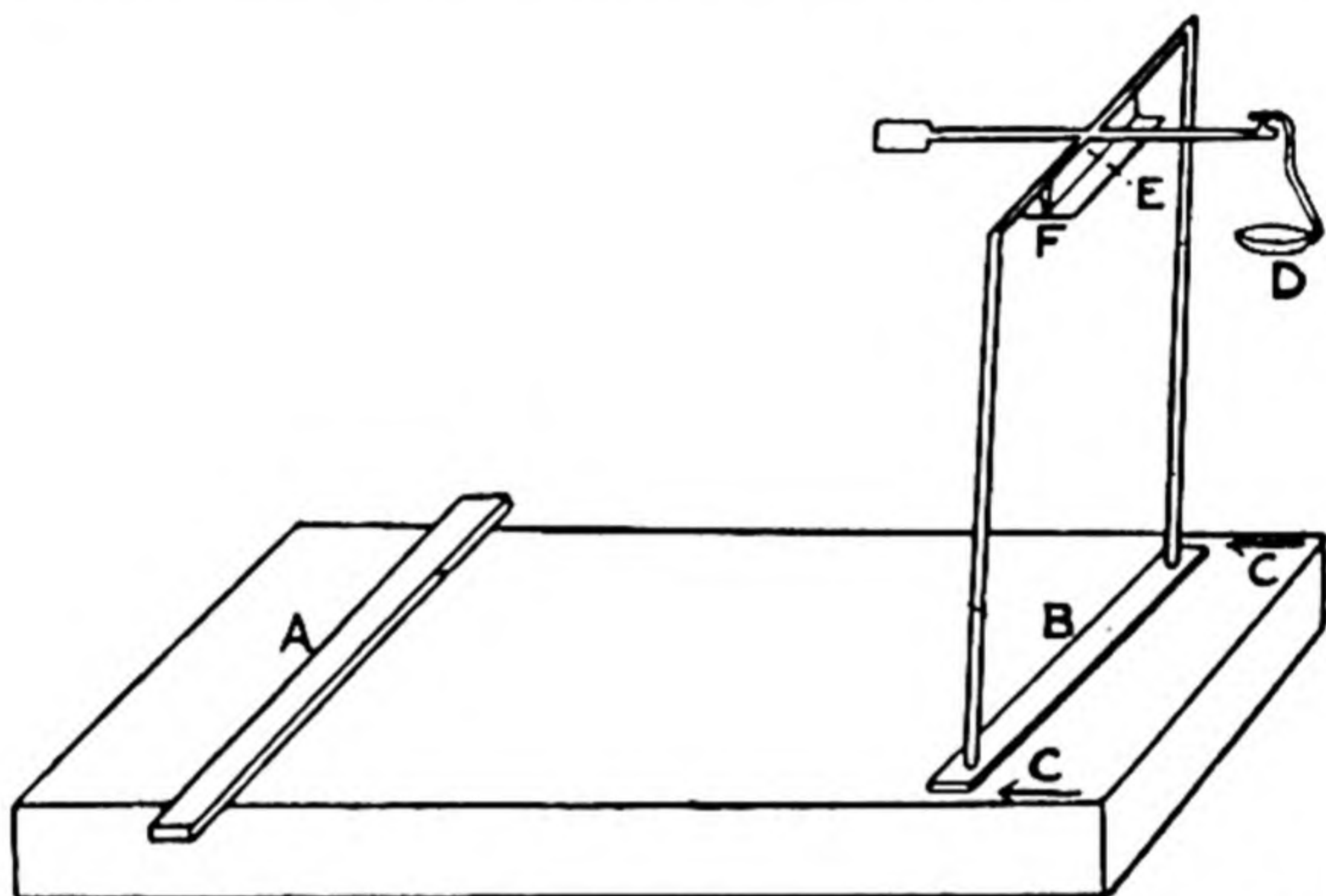


FIG. 25.—Langmuir's trough for the study of surface films of insoluble oils. *A* is a movable barrier, and *B* is a floating barrier; the oil film is enclosed between *A* and *B*. Air jets represented by *CC* prevent the oil from leaking past the barrier *B*. *D* is a balance pan, and *E* is a knife-edge which rests on a fixed support *F*. In Adam's modified apparatus (1926) the jets *CC* were replaced by thin strips of platinum foil attached to the trough and to *B*, and a torsion wire and optical lever were used instead of the arrangement *DEF*.

means of the balance. The method actually used by Langmuir was to place a definite weight on the balance pan and so displace the float; the other barrier was then brought up until the float returned to its original position. In this way the areas of the film for a given set of values of the force were determined.

**Langmuir's Observations.** The results of these experiments were plotted on a graph with the values of the surface force in dynes per cm. as ordinates and of the area occupied per single molecule as abscissæ; the latter was calculated from the measurement of the



total area of the film and a knowledge of the weight of oil on the surface, its molecular weight and the Avogadro number. The curves obtained for various substances, particularly fatty acids, were generally of the type shown in Fig. 26; when the area occupied per molecule was greater than an amount represented by the point *Q*, i.e.,  $21 \times 10^{-16}$  sq. cm.,\* the force exerted, if any, was too small to be measured on Langmuir's apparatus. From *Q* onwards, as the area was decreased, the force acting increased at first slowly and then very rapidly until the point *H* was reached (force about 60 dynes per cm.); the film which had hitherto

been invisible now commenced to crumple up, and strain lines were seen on the surface. Further compression caused the film to collapse entirely without affecting the surface force (curve *HP*). Between *Q* and a not too definite point *S* the film was liquid, because particles of dust on the surface were observed to be moving about quite freely; at *S* the film apparently becomes solid, for the dust particles lose their mobility and remain fixed. The slope of the curve *SH*

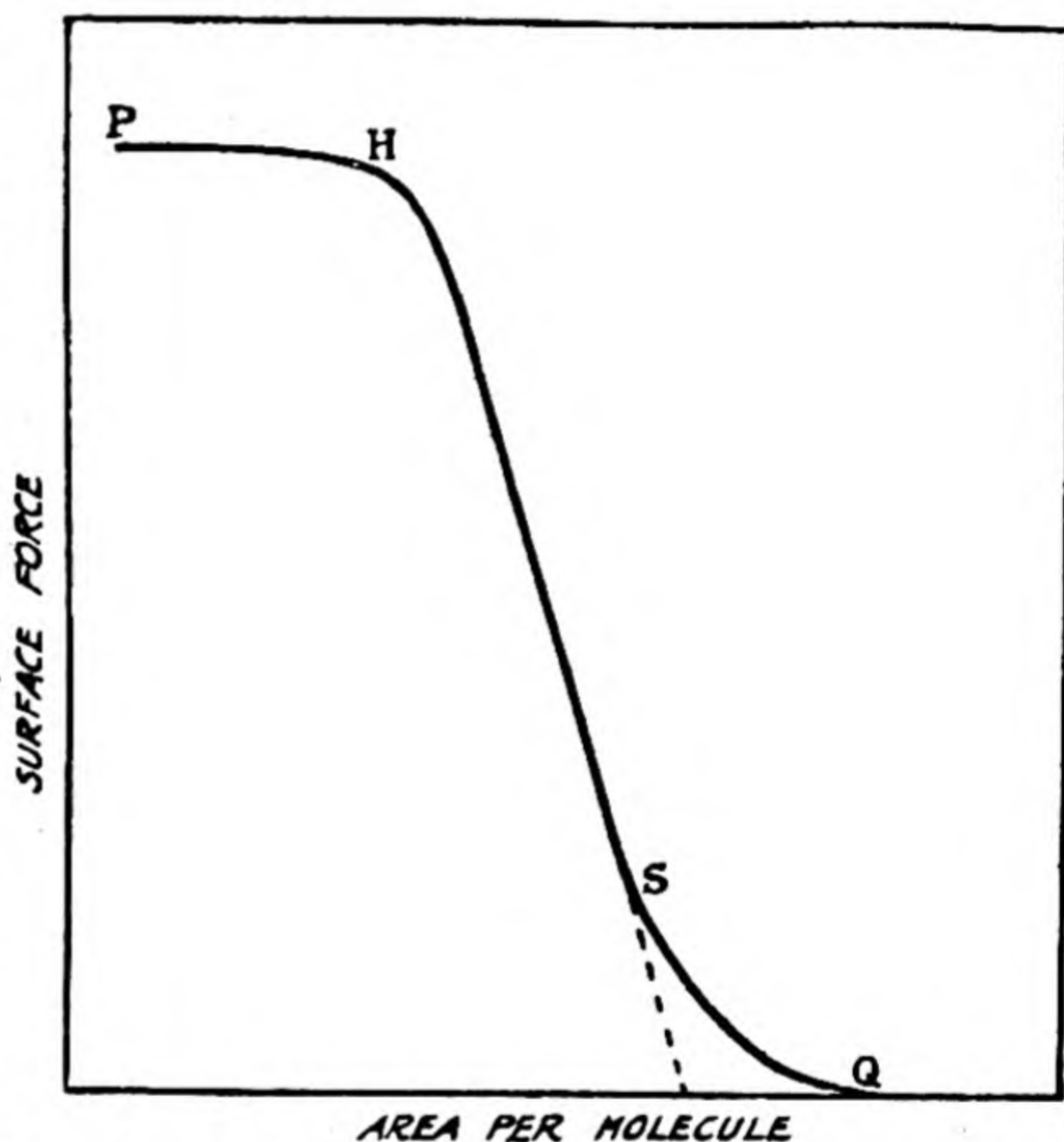


FIG. 26.—Variation of surface force with area occupied by a film of fatty acid on water; the point *Q* corresponds to an area of 21 sq. Å per molecule of acid. (After Langmuir.)

represents the compressibility of the solid film, the point *H* at which the film breaks being the limit to which compression can occur.

**The Condensed Film.** Langmuir studied the surface forces exerted by films of various fatty acids and other long chain compounds on water; some of the results were rather difficult to

\*  $1 \times 10^{-16}$  sq. cm., is often represented as 1 sq. Å, i.e., a square Ångström unit.



interpret, possibly because of impurities in the compounds used to form the films, but with saturated fatty acids, at least, the information was quite definite. For the series of acids from palmitic ( $C_{15}H_{31}\cdot COOH$ ) to cerotic ( $C_{25}H_{51}\cdot COOH$ ) the area of film occupied per molecule at the point  $Q$ , where the surface force became appreciable, was always about 21 sq. Å, independent of the length of the hydrocarbon-chain. These results are in agreement with the theory, already developed by independent arguments, of the orientation of long chain compounds with polar groups in unimolecular films. As the area of the film is decreased a condition is reached when the oriented molecules are brought so closely together that any further attempt at compression results in the exertion of an appreciable surface force; the point  $Q$  thus corresponds to the state in which the more or less vertical chains of the molecules are packed so closely together in a single layer that they begin to repel one another. The films are then said to be in the "condensed" state.

It is to be expected that the area in this state will depend mainly on the area of cross-section of the hydrocarbon-chain and not at all on its length; hence the area per molecule corresponding to the point  $Q$  should be independent of the number of carbon atoms in the fatty acid molecule. The value 21 sq. Å may thus be taken as an approximate measure of the cross-section of the  $-CH_2$  group; recent observations by means of X-rays on long chain hydrocarbons, and their derivatives, indicate that the area of cross-section of this group in a crystal is about 18.5 sq. Å. From the work of Kopp, and others, on the molecular volume of various compounds at their boiling points, it is considered that the gram-molecular volume to be attributed to a  $CH_2$  group is 22 c.c.; this is equivalent to a volume of  $36.3 \times 10^{-24}$  c.c. per single group. If the diameter of the carbon atom is assumed to be  $1.54 \times 10^{-8}$  cm., as in the diamond, the area of cross-section of the  $CH_2$  group may be calculated as approximately 28 sq. Å. The agreement of this, and the X-ray, value with that obtained from a study of oil films, on the assumption that the latter are one molecule in thickness, lends strong support to the theory of such films developed by Rayleigh and subsequent workers.



**Adam's Observations.** In 1921 Adam commenced a series of investigations which has confirmed and greatly extended Langmuir's work on films of long chain compounds; at first he used the same apparatus as had been employed in previous work, except that the waxed paper barrier was replaced by a waxed glass strip. Later (Adam and Jessop, 1926) the apparatus was considerably improved; in the first place the float was extended to within 1 mm. of the sides of the trough, and fastened to them by means of very thin strips of platinum foil. These strips were thin and light enough to exert almost no resistance to the movement of the float, but they were much more effective than the air jets in preventing leakage of the oil film. In the second place the balancing method of measuring the surface force was replaced by a torsion wire and an optical lever, so that determinations could be made down to 0.01 dyne per cm. Adam obtained force-area curves for the fatty acids which were of the same type as those of Langmuir, except that the surface forces, although small, were observed even when the film occupied fairly large areas; the point *Q*

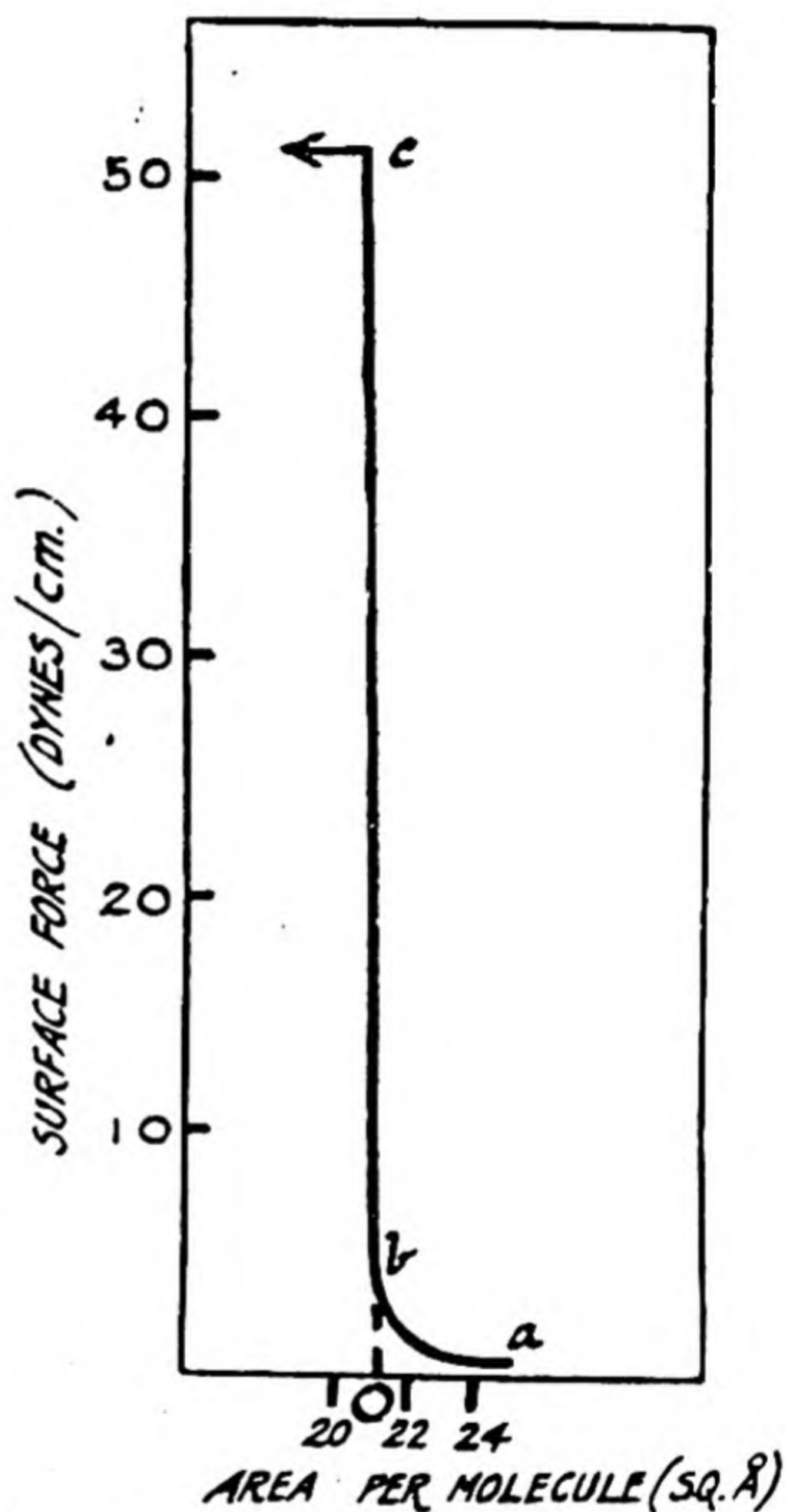


FIG. 27.—Typical force-area curve for a film of fatty acid on distilled water; the film is "condensed" in the region *b c*, and collapses at *c*. (After Adam.)

(Fig. 26) is, therefore, not as definite as Langmuir imagined. An accurate idea of the area occupied per molecule can, however, be obtained by extrapolating the straight line representing the compression of the closely packed molecules to the area axis; the result gives the area per molecule of film under zero com-



pression. A typical curve obtained by Adam is shown in Fig. 27 ; it represents the force exerted by a film of fatty acid on water at various areas per single molecule ; the line *bc* represents the compression of the condensed film, and the area for zero compression is given by the extrapolation of *bc* to *O*. The arrow at the point *c* indicates the collapse of the uniform film.

In the course of a careful examination of a large number of long chain compounds containing a variety of polar groups, it was found that although the behaviour was occasionally different at low compressions—the causes of this will be discussed later—the almost vertical portion of the force-area curves, for condensed films, was almost identical in every case. For substances containing the following polar end-groups, the minimum area occupied per molecule at zero compression was always 20.5 sq. Å, independent of the length of the hydrocarbon-chain :—

- |                      |  |
|----------------------|--|
| — COOH               | — NH·CONH <sub>2</sub> (above transition temperature)  |
| — CONH <sub>2</sub>  | — NH·CO·CH <sub>3</sub> (below transition temperature) |
| — OH                 | — COOR (monobasic esters ; R = Me, Et, Allyl).         |
| — CO·CH <sub>3</sub> | — COOC <sub>2</sub> H <sub>5</sub> (dibasic esters)    |

These results confirm the theory of the structure of oil films on water as single layers of oriented molecules with the polar groups attached to the water, and the hydrocarbon-chain more or less vertical. It does not seem possible to offer any alternative explanation for the constancy of the cross-sectional area, which is independent of the length of the hydrocarbon-chain and of the nature of the end group.

A triglyceride contains three acid residues, and hence three hydrocarbon-chains ; the glycerol portion of the molecule forms the polar end group, and so the cross-sectional area would be expected to be three times the value for a single chain, viz.,  $3 \times 20.5 = 61.5$  sq. Å, provided the three chains were aligned parallel to one another. The value found by Adam, 63.0 sq. Å, is in further confirmation of the general theory, although in crystals of triglycerides the chains are probably not arranged in the



manner postulated (Clarkson and Malkin, 1934). Molecules of aromatic compounds with  $-\text{C}_6\text{H}_4\cdot\text{OH}$ ,  $-\text{C}_6\text{H}_4\cdot\text{NH}_2$  or  $-\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}_3$  as end groups have a cross-sectional area, at zero compression, of about 24 sq. Å. These substances must orient themselves with the  $-\text{OH}$ ,  $-\text{NH}_2$  or  $-\text{CO}\cdot\text{CH}_3$  group in the water, and hence the size of the benzene nucleus is probably the deciding factor in the packing of the molecules; the cross-sectional area of the nucleus must therefore be 24 sq. Å. This value agrees approximately with that of the effective cross-section of a benzene ring in a crystal lattice, calculated from X-ray measurements.

#### Films on Dilute Acid.

In the course of his studies Adam made a more complete investigation of a curious phenomenon observed by Langmuir with films of various saturated acids on dilute hydrochloric acid, instead of water; the force-area curves for the condensed films were of the type shown in Fig. 28. The portion  $cd$  representing the film in its state of closest packing is the same as for films on water; on extrapolating to zero compression ( $O_2$ ) the area per molecule is still 20.5 sq. Å. The portion  $bc$  of the

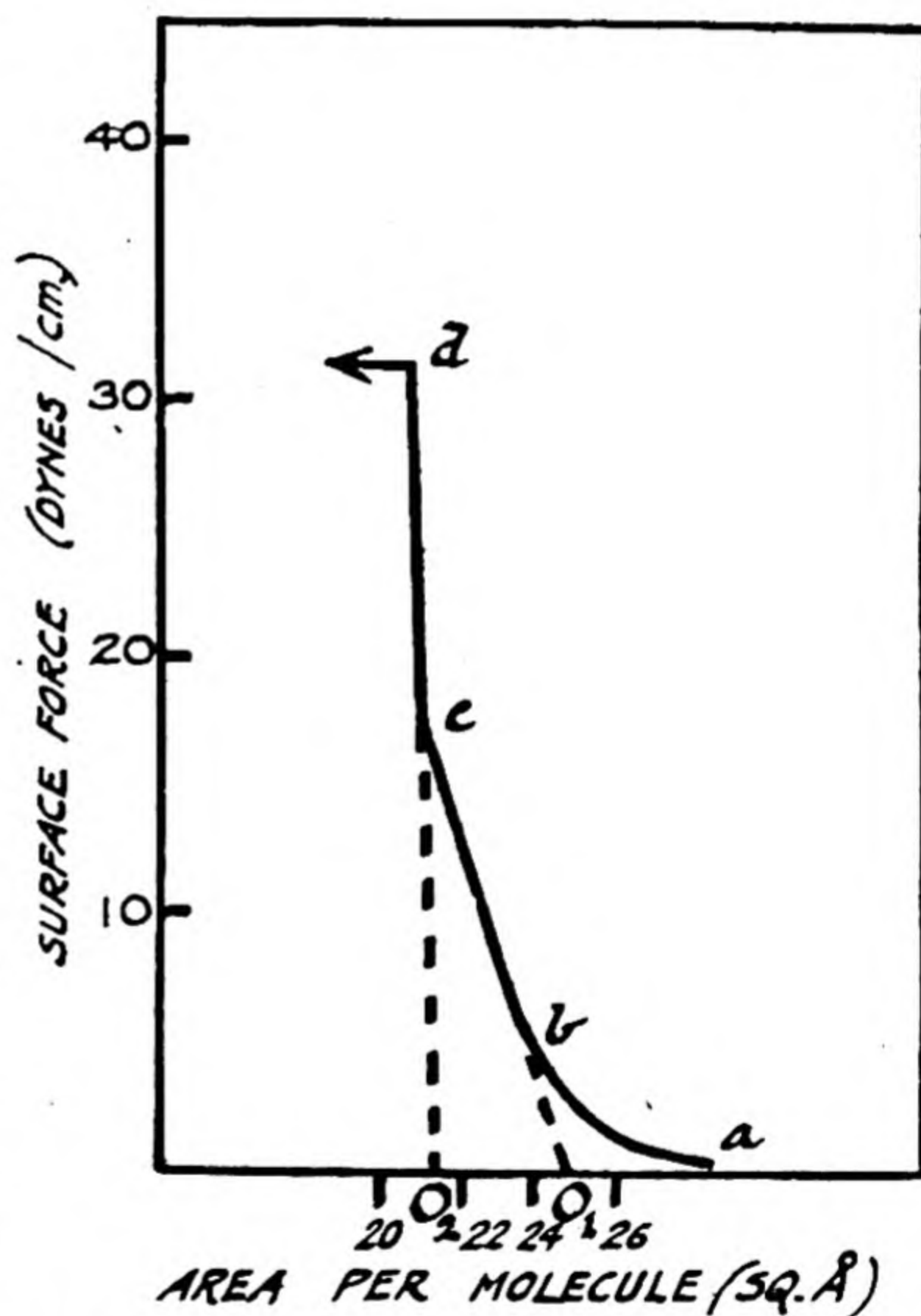


FIG. 28.—Force-area curve for a film of a fatty acid on 0.01 N-hydrochloric acid. (After Adam.)

curve does not occur with fatty acids on pure water; extrapolation of this curve to  $O_1$  gives the area per molecule, independent of the length of the hydrocarbon-chain, as 25.1 sq. Å. To explain these results Adam has suggested, that owing to the acidity of the



aqueous layer there is a slight tendency for the  $\text{—COOH}$  groups to be repelled from it, so that the first break in the curve represents the condition at which the "heads" of the molecule, *i.e.*, the carboxyl groups, are packed as closely as possible (Fig. 29, A); the area of cross-section of the  $\text{—COOH}$  group, on this theory, is then  $25.1 \text{ sq. \AA}$ . On further compression the molecules rearrange themselves by pushing the end-groups further into the water and interlocking, so that the hydrocarbon-chains are closely packed (Fig. 29, B); the completion of this packing gives the second break in the force-area curve, and the area occupied per molecule is the normal value for the hydrocarbon-chain ( $20.5 \text{ sq. \AA}$ ). By studying fatty acid films on a series of solutions, Adam and Miller (1933) found that the change from the close-packed chain to the close-packed head type of structure occurred within a small range of  $pH$ , generally between 6 and 8. In strongly alkaline solutions the area of closest packing is increased to over  $30 \text{ sq. \AA}$ ; this is attributed to adsorption of cations by the heads.

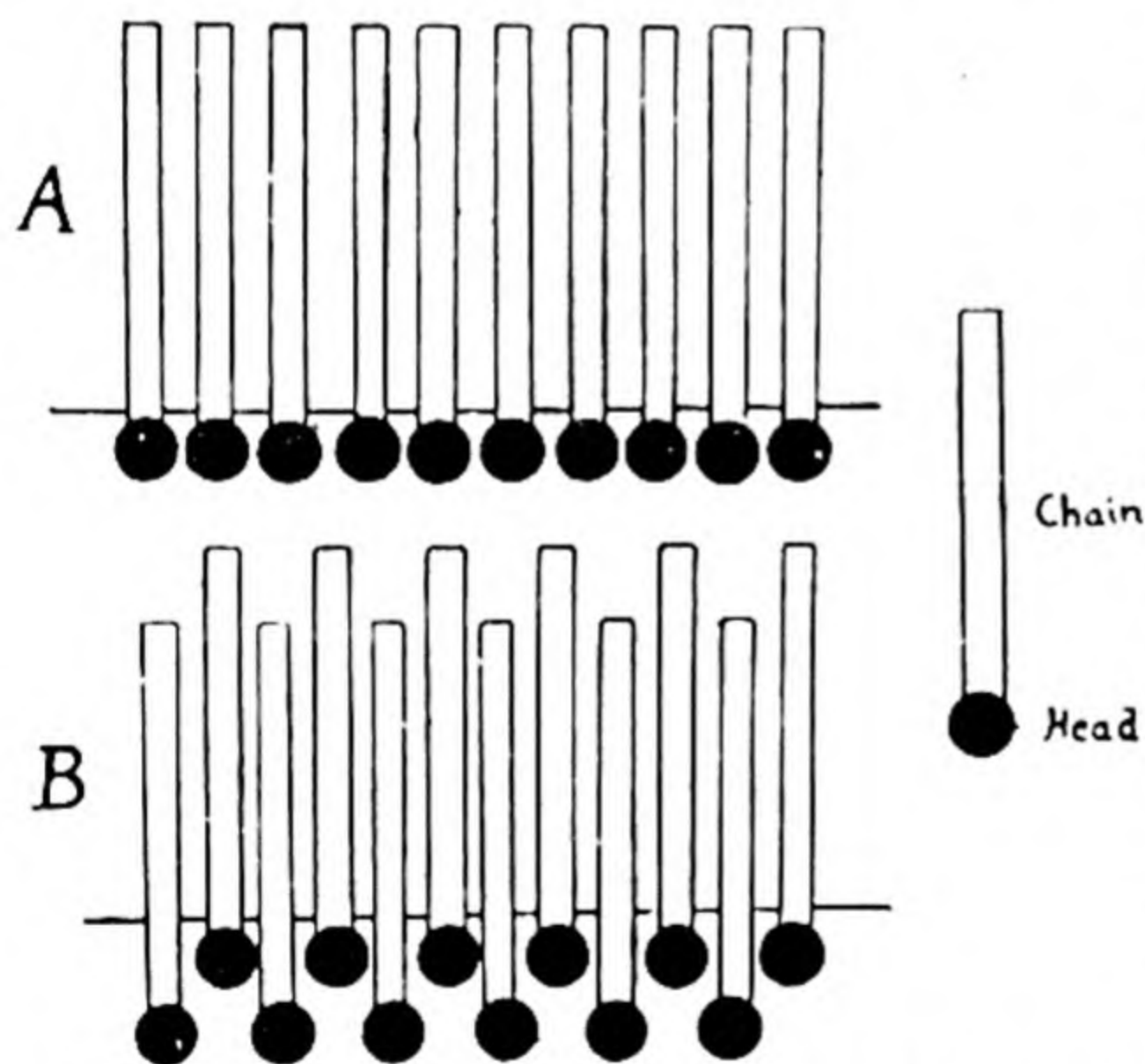


FIG. 29. — Diagrammatic representation of Adam's suggestion of "close-packed heads" (A) and of "close-packed chains" (B), in a unimolecular film of fatty acid on a dilute aqueous solution of hydrochloric acid.

Curves similar to those given by fatty acids on dilute hydrochloric acid have been obtained for long chain alcohols (first break at  $21.6^* \text{ sq. \AA}$ ) and esters (first break at  $22.0 \text{ sq. \AA}$ ) on water; in each case the first break—"close packed heads"—ascribed by Adam to the area of the end-group, varies with the nature of the group, but the second break—"close packed chains"—extrapolated to zero compression, was the same in

\* The cross-sectional area of the  $\text{—CH}_2\text{OH}$  group has been found to be  $22.1 \text{ \AA}^2$  by X-ray measurements (Marwick, 1931).



every case. In the films of acids, alcohols and esters, therefore, it has been suggested that the "close packed heads" can be made to rearrange by increasing the compression, but this rearrangement is apparently not always possible. As already mentioned, *p*-derivatives of benzene have an area of 24 sq. Å per molecule, but this cannot be at all decreased on further compression; the same applies to nitriles, for which the cross-sectional area of 27.7 sq. Å per molecule is attributed to the —CN group.

Long-chain derivatives of urea (end-group —NH·CONH<sub>2</sub>) and of acetamide (end-group —NH·COCH<sub>3</sub>) have a curious type of intermediate behaviour; above a certain transition temperature in the former case, and below a transition point in the latter, the substances give simple force-area curves like those of a fatty acid on water (Fig. 27) with a limiting area of 20.5 sq. Å, but on the other side of the transition point the areas are 26.0 and 24.2 sq. Å, respectively, per molecule.

**Solid and Liquid Films.** Rideal and Lyons (1929) have suggested a modification of Adam's views concerning the close packed heads and chains; he considers that the portion *cd* (Fig. 28) extrapolating to 20.5 sq. Å, always represents a *solid* condensed film, whereas *cb* may indicate the compressibility of the *liquid* film. In the solid film the molecules are held together, more or less rigidly, by forces of the crystal lattice and the area of cross-section per molecule should be constant and definite. The question arises, however, as to why the area of cross-section of the molecule in the solid fatty acid film (20.5 sq. Å) is not identical with the value determined from X-ray studies of the crystals, for example, of stearic acid (18.4 sq. Å). To overcome this difficulty Rideal and Lyons (1929) have suggested that the oriented molecules in the solid film are all tilted at a definite angle to the surface of the water. Müller (1928) established definitely that hydrocarbon-chains consist of a series of zigzags in one plane, and it is assumed by Rideal that when the zigzags of adjacent molecules correspond exactly to one another, so that interlocking is possible, a condition of great stability is reached. Strictly speaking such interlocking should occur readily with the molecules vertical, but since the polar group is attached



asymmetrically to the end of the hydrocarbon-chain, when the former is attracted into the water the latter must be tilted. Even if the chains are not vertical, interlocking can occur again when each molecule is tilted through an angle of about  $27^\circ$  to the vertical; in this state a very stable film should be formed. Assuming the molecular spacing in the film to be the same as in crystals of stearic acid, the area of cross-section of the molecule in the film parallel to the water surface, or in other words the area occupied per molecule with a tilt of  $27^\circ$ , can be calculated as 20.6 sq. Å, in excellent agreement with the measured value for a condensed film.

Adam has pointed out, however, that in the high compression state (*bc*, Fig. 27) the films are sometimes solid and sometimes liquid, as indicated by the movement of talc or lycopodium particles sprinkled on the surface, but the area per molecule is always the same, 20.5 sq. Å. With the long chain alcohols, for example, the areas in the high pressure state are constant from  $C_{11}$  onwards, yet the films are still liquid at  $C_{20}$ ; according to the theory of Lyons and Rideal all these films should be solid when the area is 20.5 sq. Å per molecule. Schulman and Hughes (1982), working in Rideal's laboratory, have found that certain alcohols, *e.g.*, hexadecyl ( $C_{16}$ ) and eicosyl ( $C_{20}$ ), give force-area curves of the type shown in Fig. 28, yet the film may be liquid in *both* states *bc* and *cd*; this is directly opposed to the theory that *cd* represents a solid film. The authors state that a reconsideration of the case—presumably for the theory of Rideal and Lyons—is necessary, and in the meantime use the non-committal titles of  $\alpha$ - and  $\beta$ -condensed films to designate the two states. None of the results obtained from force-area curves, or from a study of surface potentials (p. 370), however, appears to contradict Adam's theory of close-packed heads and chains.

### EXPANDED FILMS

In 1921 Labrouste observed that increase of temperature sometimes produces a marked change in the area of a surface film; this phenomenon was subsequently investigated by Adam and others.



If the temperature of a film of fatty acid on dilute hydrochloric acid is raised gradually, and its compression kept constant, the area remains at first unchanged, but at a certain temperature it commences to increase rapidly; this increase extends over a range of  $5^{\circ}$  to  $15^{\circ}$ , until an area roughly two or three times the original value is attained. The film is then in the "expanded" state, and further increase of temperature produces a small but steady increase in the area at constant compression. The temperature at which expansion of a given film commences is raised if the compression of the film is increased. In any homologous series each additional  $\text{CH}_2$  group raises the temperature at which the condensed film changes to an expanded one by about  $7^{\circ}$  to  $10^{\circ}$ . The expansion temperatures of films of fatty acids and of other substances with ionisable end-groups decrease considerably if the underlying aqueous medium is made definitely alkaline. The development of similar electrical charges on adjacent molecules causes a repulsion which diminishes the lateral adhesion of the molecules. The effect of various ions shows, however, that this is not the only factor operative (Adam and Miller, 1938).

**Liquid and Vapour Expanded Films.** Expanded films may be roughly divided into two types—liquid and vapour—although the line of demarcation between them is not very definite. Liquid expanded films generally tend towards a more or less definite area at zero compression, measured in the vicinity of the expansion temperature; this area is of the order of twice the value for the condensed film. For example, in his early work (1917) Langmuir found that an oleic acid molecule occupied an area of about  $46 \text{ sq. \AA}$ ; later it was found that such films are generally expanded, and the approximately double value of the area could be accounted for. One of the chief characteristics of liquid expanded films is that they have a range of definite "surface vapour pressure" (see Fig. 30); that is, like a liquid, they exert a definite force (pressure, for liquid) irrespective of the area covered (volume occupied, for liquid), within certain limits. In this state they may be regarded as behaving like saturated vapours. Fatty acids, nitriles, alcohols, amides, ureas and acetamides form such films. Vapour expanded



films have no definite limiting area, nor do they have a constant surface pressure, but pass without discontinuity into "gaseous" films, to which reference will be made later. Esters, methyl ketones and acetates capable of forming surface films pass from the liquid condensed state directly to the vapour expanded form on heating. It appears that there is a certain critical temperature above which liquid expanded film does not exist under any surface pressure, and that for the vapour expanded film the expansion temperature is, under the experimental conditions, above this value.

Langmuir (1925, 1933) and Schofield and Rideal (1926) suggested that expanded films consist of an arrangement of tilted molecules in which the chains tend to adhere to some extent, but the heads are free to move on the surface of the water. At low compressions an increase of temperature increases the thermal agitation of the molecules so that a condensed film passes into an expanded one. It should be mentioned also that the molecules in the liquid film must be regarded as hinged, rather than rigid, chains since there is free rotation about single bonds; an increase of temperature will no doubt increase the extent of agitation within the molecule itself. Adam is of the opinion that since it is the nature of the head which determines whether the expanded film is of the liquid or vapour type, it is the heads which tend to hold together, but the chains are supposed to tilt away from one another in the formation of an expanded film. It appears, in favour of this point of view, that when the heads attract one another strongly, *e.g.*,  $-\text{COOH}$  and  $-\text{OH}$ , liquid expanded films are formed, but when the attraction is not so great, *e.g.*,  $-\text{COOC}_2\text{H}_5$ ,  $-\text{CO}\cdot\text{CH}_3$ , vapour films result. The latter are supposed to be formed when the heads, as well as the chains, tend to break away from one another. Langmuir has pointed out that since the head groups are the cause of the spreading of an oil on water it is to be expected that these groups will try to cover as large an area as possible; expansion will result when the thermal agitation allows the free movement of the end groups, whilst the chains still tend to adhere to one another. It should be noted that the mutual attraction of two  $-\text{COOH}$  groups, as observed in the crystals of fatty acids, is probably due to the fact that in such cases there is a stable



arrangement of dipoles (Müller, 1929); this type of arrangement does not seem possible if the hydrocarbon chains are placed side by side. Rideal has indicated another argument in favour of the

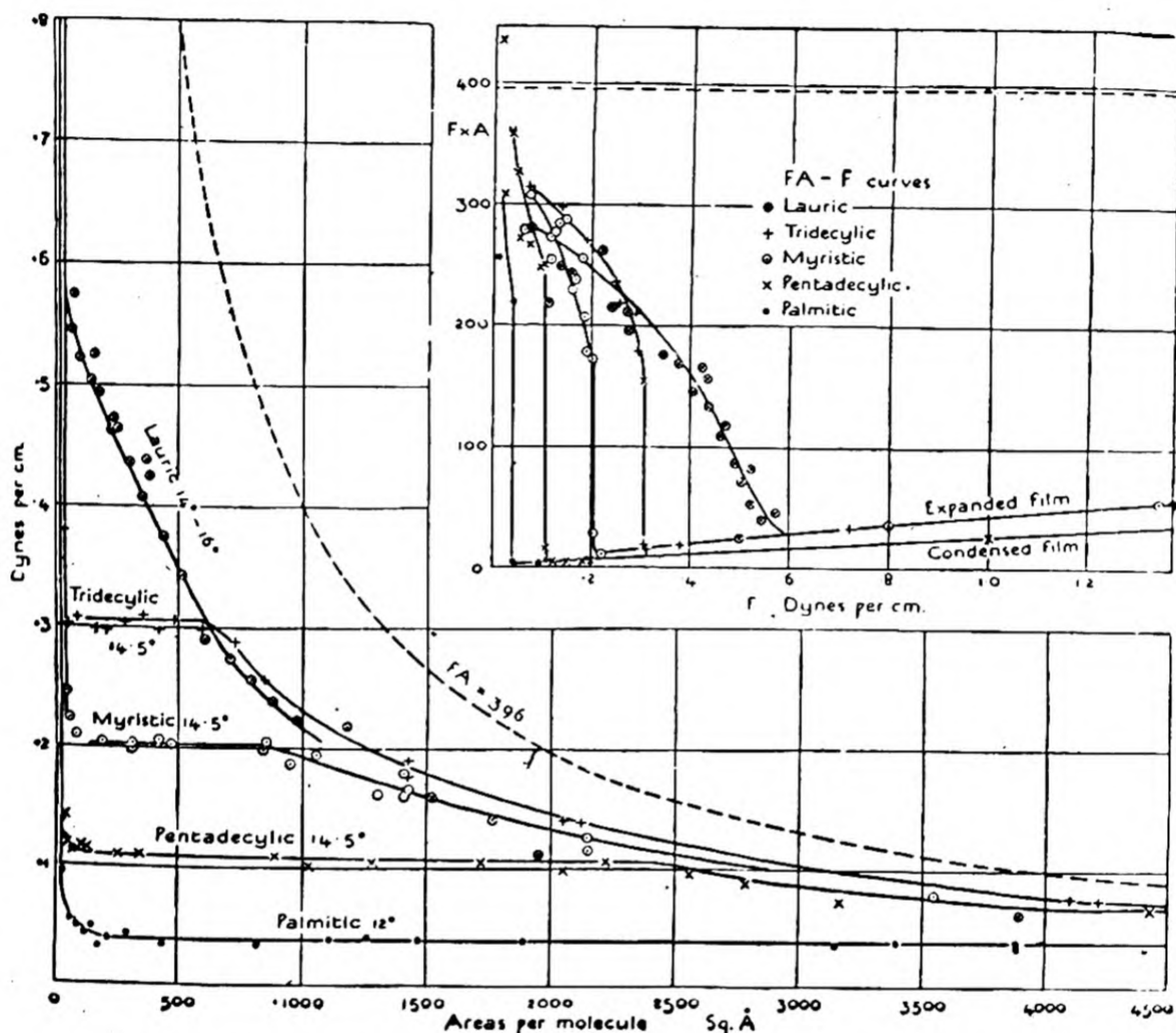


FIG. 30.—Force-area curves for fatty acid films at low compressions on 0.01 *N*-hydrochloric acid. Palmitic and pentadecylic acids form liquid condensed films at the temperatures indicated; these have a definite “surface vapour pressure” and pass discontinuously into gaseous films. Myristic and tridecylic acids form liquid expanded films at 14.5° on dilute acid, and these also have a definite “vapour pressure.” Lauric acid at 14–16° forms a vapour expanded film. (From Adam’s “Physics and Chemistry of Surfaces.”)

Langmuir theory of the expanded film: if the heads adhered and not the chains then the effective area per molecule should be greater the longer the chain; but if the reverse were the case the



longer the chain the greater the adhesion, and so the smaller the area covered per molecule. The earlier results obtained by Adam suggested that in the liquid expanded film the area became smaller as the chain was lengthened, but later he concluded that the area was more or less independent of the number of  $\text{CH}_2$  groups. Further investigation of this point with the sensitive apparatus now available appears to be desirable.

**Gaseous Films.** Both types of expanded film at elevated temperatures, or at very low compressions, that is at large areas of the order of 5000 sq. Å per molecule, are converted into gaseous films. The investigation of such films was only rendered possible as a result of the improvement by Adam and Jessop of the apparatus for the study of surface films; with the original form the very small surface pressures could not have been measured. With liquid expanded films there is a discontinuous transition which occurs at an area dependent on the temperature. The force-area curves for the change from a liquid expanded to a gaseous film bear a very striking resemblance to the pressure-volume curves, such as those obtained by Andrews, for the liquefaction of a gas like carbon dioxide (Fig. 30). As already mentioned, vapour expanded films pass gradually into gaseous films without any discontinuity. Some substances, *e.g.*, esters of dibasic acids, and fatty acids on dilute alkali, expand from the condensed to the gaseous state with only a very slight intermediate condition in which the films are of the vapour expanded type.

**Two-Dimensional Gases.** Adam (1926) has shown that the analogy between two-dimensional gaseous films exerting surface pressure and ordinary gases exerting gas pressure is very striking. The surface pressure is regarded as the force, in dynes per cm., due to the film, measured in the ordinary manner; in other words, the surface pressure is equal to the compression of the film. If the product of the surface pressure ( $F$ ) and the area per molecule ( $a$ ) for a gaseous film is plotted against the surface pressure, the resulting curves, for many substances, show a marked resemblance to the  $pv-p$  curves obtained for a gas like nitrogen at ordinary temperatures. For substances which yield liquid expanded films the  $Fa-F$  curves, as already implied in the previous paragraph,



resemble the  $pv$ — $p$  curves for an easily liquefiable gas like carbon dioxide. The resemblance between gaseous films and ordinary gases is, however, quantitative as well as qualitative. If the long chain molecules are assumed to be quite insoluble in water, but to have sufficient adhesion to water to prevent them evaporating, and the surface pressure is considered to be due to the bombardment by the molecules moving freely in the surface, then the value of this pressure may be determined by an application of the same methods as are used in the kinetic theory of gases. In a perfect gaseous film the long chains should have no lateral adhesion for one another, and the total area of cross-section of the molecules should be negligible in comparison with the total area of the film; then if the kinetic energy of translation is  $\frac{1}{2}kT$  for each of the two degrees of freedom (three in ordinary gases) it may be shown that

$$Fa = kT \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (\text{xiv.})$$

where  $k$ , equal to  $R/N$ , is the Boltzmann gas constant per molecule ( $R$  is the ordinary gas constant, and  $N$  is the Avogadro number),  $F$  is the surface force in dynes per cm., and  $a$  is the area of the film per molecule of long chain compound. This equation is, of course, quantitatively analogous to the ordinary gas equation, the constant  $k$  having exactly the same value, namely  $1.372 \times 10^{-16}$  ergs per degree. At ordinary temperatures, when  $T$  is about  $290^\circ$ ,  $kT$  is approximately  $400 \times 10^{-16}$  ergs, and so according to the theory  $Fa$  should always have this value. In actual practice, however, it is only so at very small surface pressures, just as for ordinary gases  $pv$  is approximately constant only when the pressure is low. For the majority of gaseous films  $Fa$  rapidly decreases as the surface pressure is increased, owing to the lateral attraction of the hydrocarbon-chains; with further compression the value of  $Fa$  decreases very suddenly as the gaseous film changes into one of the liquid expanded type. The deviation from ideal behaviour increases as the hydrocarbon-chain becomes longer, and so there is strong evidence for the view (p. 366) that these chains do attract one another laterally.

There is good reason to believe that in the gaseous film the molecules probably lie more or less flat on the surface. Langmuir has shown that in very dilute solutions of the more soluble fatty



acids the work of adhesion per molecule of acid increases by a definite amount for each  $\text{CH}_2$  group added to the chain; every  $\text{CH}_2$  has therefore the same relation to the water surface, and this can only be so if the molecules lie flat in the surface. It will be shown later that the surfaces of these dilute solutions of soluble acids resemble closely the gaseous films of insoluble substances; hence it is probable that in the latter the molecules also lie flat in the surface. It may appear at first sight that this view is not in harmony with the idea that polar groups cause a definite orientation with reference to the surface. As a matter of fact, the work of adhesion (p. 347) between a hydrocarbon and water is almost the same as the work of cohesion of the hydrocarbon itself; there will, therefore, be just as much tendency for the hydrocarbon-chain to be on the water as for two chains to adhere to one another. It is only when the film is under compression that orientation, with the resulting decrease of free energy, occurs; the same difference applies to the adsorbed surface layers in solutions of comparatively soluble fatty acids. Another argument in favour of the view that the molecules in a gaseous film lie flat on the surface is the fact, observed by Adam, that compounds having polar groups at both ends, *e.g.*, esters of dibasic acids, form such films very readily. It is easy to understand that with two water attracting groups separated by a hydrocarbon-chain the molecule will have a strong tendency, at low surface pressures, to lie flat on the water surface.

### SURFACE POTENTIALS

A new technique for the study of surface films, first introduced by Guyot (1924) and Frumkin (1924), has been developed by Schulman and Rideal (1931) and improved by Adam and Harding (1932) and Schulman and Hughes (1932). By coating a platinum wire with a radioactive material the air between the wire and a surface film can be rendered ionised and conducting; if the "air electrode" so formed and an ordinary standard calomel, or silver-silver chloride, electrode dipping in the liquid of the experimental trough (Fig. 25) are connected to an electrometer the *E.M.F.* indicated includes the potential difference at the air-liquid inter-



face. If this *E.M.F.* is measured in the absence of a surface film and then with one present the difference in the values, called  $\Delta V$ , is related to the number of molecules per sq. cm. of film,  $n$ , by the equation, due to Helmholtz :

$$\Delta V = 4\pi n\mu,$$

where  $\mu$  is the average effective vertical component of the dipole moment of the surface film-forming molecules. The value of  $\mu$  may only be remotely connected with the normal value of the dipole moment (Chapter III.), since it is not only a vertical component and so dependent on the orientation of the polar group, but it also includes all effects due to the re-distribution of ions in the solution and to the re-orientation of water molecules ; it does, however, in spite of lack of knowledge concerning its exact significance, provide useful information about the structure of surface films. By varying the area covered with the unimolecular surface film, with moving barriers in the ordinary way (p. 355), it is possible to measure  $\Delta V$ , and so calculate  $\mu$ , for various values of the area per molecule of film-forming substance. A combination of the force-area apparatus with that for potential-area measurement makes it possible to correlate the state of the film with the corresponding potential difference at the air-liquid interface.

**Liquid Expanded Film.** In a study of myristic acid, which during compression at ordinary temperatures changes from a gaseous, through a "saturated vapour" (p. 365), to a liquid expanded film, on 0.01 *N*-hydrochloric acid, Adam and Harding found that corresponding exactly to the marked inflexion in the force-area curve at 47 Å<sup>2</sup> per molecule, where the saturated vapour changes to the completely liquid film, there was a definite change in the surface potential. The value of  $\mu$  in the completely liquid film falls immediately by about one-half when vaporisation commences at 47 Å<sup>2</sup>. This change must correspond to a definite change in the orientation of the molecules in the surface ; in the liquid film the molecules are more or less vertical, but in the vapour film some will be flat and so the vertical component of the dipole moment will be reduced. With dibasic esters having carbethoxy-



groups at opposite ends of the chains, on the other hand,  $\mu$  is greater when the molecules lie flat, in the gaseous film, than when they are vertical, in the condensed state (Adam *et al.*, 1925).

Further confirmation of the structure of the surface film in the saturated vapour state, corresponding to the horizontal lines in Fig. 30, was obtained from the observation that with this type of film the surface-potential measurements were very erratic; if the air electrode were kept stationary, variations in the potential were found and different results were obtained by moving the electrode. Similar observations have been made by Harkins and Fischer (1933). These fluctuations, which are probably due to the movements of "pools," or "islands," of coherent, liquid expanded film over the surface, ceased at areas greater than about  $800 \text{ \AA}^2$ ; this corresponds almost exactly to the area, found by Adam and Jessop (see Fig. 30), at which the surface film becomes wholly gaseous and consequently uniform.

At high compressions the liquid expanded film passes over gradually into a condensed film, but no appreciable break in the potential-area curve was found to correspond to this transition, and the values of  $\mu$  ( $2.26\text{--}2.15 \times 10^{-19}$  e.s.u.) showed very little change. It must be concluded, therefore, that the orientation of the  $-\text{COOH}$  group, which is mainly responsible for the dipole moment, remains constant with regard to the surface of the water in spite of the changes in the type of film covering the surface. With alcohols, methyl ketones and aldoximes, it has also been noted that there is no appreciable change in the value of  $\mu$  during the transition from expanded to the condensed state (Adam *et al.*, 1935). Adam and Harding interpret these results as favouring the view that in the expanded film the end-groups tend to adhere and that the chains rotate about the C—C linkages; the area per single molecule may thus change although the effective vertical dipole moment will remain constant.

**Condensed Films.** With palmitic ( $\text{C}_{16}$ ), stearic ( $\text{C}_{18}$ ) and behenic ( $\text{C}_{22}$ ) acids the vapour film on compression passes through the saturated vapour stage and then directly to the condensed state; in these cases the potential showed a definite change at an area of about  $25 \text{ \AA}^2$  per molecule, corresponding to the break in the force-



area curve (Fig. 28) for films of these fatty acids on 0.01 *N*-hydrochloric acid. The reduction in the value of  $\mu$  and the fluctuations observed during the evaporation of the condensed film are in harmony with the views already expressed concerning the nature of the saturated vapour and gaseous states. In passing from one type to the other of the states represented by *bc* and *cd* in Fig. 28, *i.e.*, Adam's close-packed heads and chains, no appreciable change in the value of  $\mu$  was observed; further, this value was almost the same, *viz.*,  $2.2-2.4 \times 10^{-19}$  e.s.u., as that found for a liquid expanded film such as myristic acid. It appears, therefore, that the orientation of the dipolar group is the same in both condensed and expanded films, the difference in area per molecule being determined by the extent to which the hydrocarbon-chains are able to rotate about various C—C linkages.

### GASEOUS FILMS OF SOLUBLE SUBSTANCES

By differentiating Szyszkowski's equation (p. 353) representing the variation of the surface tension of aqueous solutions of fatty acids with the concentration, it is found that

$$d\gamma = -\frac{B\gamma_0}{2.302} \cdot \frac{dc}{c+A} \quad \dots \dots \dots \text{(xv.)}$$

$$\therefore \frac{d\gamma}{dc} = -\frac{B\gamma_0}{2.302(c+A)} \quad \dots \dots \dots \text{(xvi.)}$$

Substituting for  $d\gamma/dc$  in the Gibbs adsorption equation (p. 351) it follows that

$$\Gamma = \frac{B\gamma_0}{2.302 RT} \cdot \frac{c}{c+A} \quad \dots \dots \dots \text{(xvii.)}$$

For very dilute solutions *c* may be neglected in comparison with *A*, and therefore

$$\Gamma = \frac{B\gamma_0}{2.302 RT} \cdot \frac{c}{A} \quad \dots \dots \dots \text{(xviii.)}$$

Since *B*,  $\gamma_0$ , *R*, *T* and *A* are all constant,  $\Gamma$  is directly proportional to the concentration of the solution; hence from the Gibbs equation it follows that  $d\gamma/dc$  is a constant under these conditions.



In other words, the surface tension is a linear function of the concentration, and so it is possible to write

$$-\frac{d\gamma}{dc} = \frac{\gamma_0 - \gamma}{c} \quad \dots \quad (\text{xix.})$$

where  $\gamma_0$  is the surface tension of pure water and  $\gamma$  that of the solution of concentration  $c$ . Writing  $F$  for  $\gamma_0 - \gamma$ , and substituting once more in the Gibbs equation, there is obtained the relationship

$$F = RT \Gamma \quad \dots \quad (\text{xx.})$$

If  $a$  is the area occupied per molecule in the surface, then  $Na$  is the area per gm. mol. ( $N$  is the Avogadro number), and this is equal to  $1/\Gamma$ , since  $\Gamma$  is the number of gm. mols. per unit area. Hence provided the solution is dilute

$$Fa = \frac{R}{N} T = kT \quad \dots \quad (\text{xxi.})$$

where  $k$ , as before, is the Boltzmann gas constant. This equation is of exactly the same type as that deduced for the so-called gaseous surface films of insoluble substances. A method for testing the applicability of this equation to surface layers of soluble substances was devised by Rideal and Schofield (1925). The Gibbs equation may be written in the form

$$\Gamma = \frac{1}{RT} \cdot \frac{d(-\gamma)}{d \ln c} \quad \dots \quad (\text{vi.b})$$

and since  $\gamma_0$  is a constant,

$$\Gamma = \frac{1}{RT} \cdot \frac{d(\gamma_0 - \gamma)}{d \ln c} \quad \dots \quad (\text{xxii.})$$

$$= \frac{1}{RT} \cdot \frac{dF}{d \ln c} \quad \dots \quad (\text{xxiii.})$$

$$= \frac{F}{RT} \cdot \frac{d \ln F}{d \ln c} \quad \dots \quad (\text{xxiv.})$$

Since  $\Gamma = 1/Na$ , then

$$\frac{FNa}{RT} = \frac{d \ln c}{d \ln F} \quad \dots \quad (\text{xxv.})$$

$$\text{or } \frac{Fa}{kT} = \frac{d \ln c}{d \ln F} \quad \dots \quad (\text{xxvi.})$$



If equation (xxi.) holds then  $Fa/kT$  should be equal to unity, and if  $Fa/kT$  is plotted against  $F$ , a line parallel to the  $F$  axis should be obtained; alternatively it follows from equation (xxvi.) that plotting  $d\ln c/d\ln F$  against  $F$  is the same as plotting  $Fa/kT$  against  $F$ , and the same straight line should result. Using the measurements of Szyzskowski and of Frumkin on the surface tension of aqueous solutions of butyric, valeric and caproic acids, Rideal and Schofield have calculated the values of  $d\ln c/d\ln F$  and plotted the

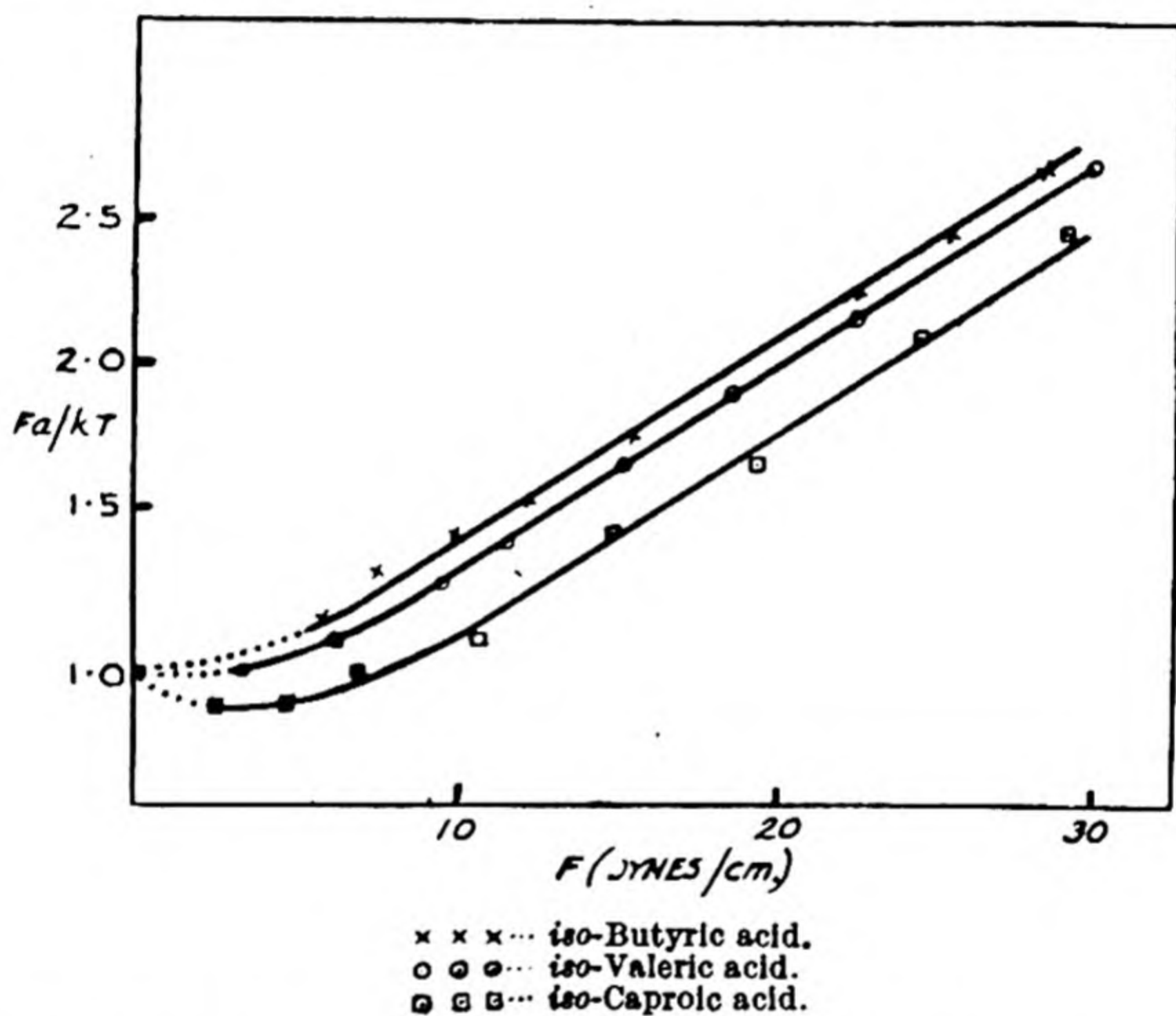


FIG. 31.—Test of the gas law equation for surface films of aqueous solutions of fatty acids; the curves should be horizontal for an ideal film. (After Schofield and Rideal.)

results against  $F$ ; the graphs obtained (Fig. 31) were not parallel to the  $F$  axis, showing that surface layers do not obey an equation of the gas-law form. The curves were, however, of exactly the same type as the  $pv-p$  curves for nitrogen, indicating that the molecules in the surface attract one another in the same way as do gaseous molecules. The initial dip in the  $Fa/kT$  against  $F$  curve was found to increase, indicating greater adhesion between the molecules, as the length of the hydrocarbon-chain increased.



$$p(v - b) = RTx \quad . \quad . \quad . \quad . \quad . \quad . (\text{xxvii.})$$
$$pv = pb + RTx \quad . \quad . \quad . \quad (\text{xxvii.a})$$
$$Fa = Fb + kTx \quad . \quad . \quad . \quad . \quad . \quad (\text{xxviii.})$$

$$\therefore \frac{Fa}{kT} = \frac{Fb}{kT} + x \quad . \quad . \quad . \quad . \quad . \quad . \quad (\text{xxix})$$

TABLE LXI.—*Amagat's Equation applied to Surface Layers*

Substance.	$\delta$ (sq. cm.).	$\epsilon$ .
<i>n</i> -Butyric acid . .	$24.3 \times 10^{-16}$	0.73
<i>n</i> -Valeric acid . .	„	0.63
<i>n</i> -Caproic acid . .	„	0.43
<i>iso</i> -Butyric acid . .	$25.1 \times 10^{-16}$	0.78
<i>iso</i> -Valeric acid . .	„	0.68
<i>iso</i> -Caproic acid . .	„	0.48

The constancy of the  $b$  values, irrespective of the length of the hydrocarbon-chain of the acid, implies that as the concentration



of the solution increases the molecules in the surface become oriented perpendicularly to that surface, so that the limiting area occupied is independent of the chain length. The decrease in  $\alpha$  with increasing chain suggests that the hydrocarbon-chains tend to adhere, and that the force of adhesion is greater the longer the chain of  $\text{CH}_2$  groups. The values of the limiting areas ( $b$ ) per molecule are in good agreement with one another and with those generally accepted, and a more comprehensive investigation by Kosakewitsch and Uschakowa (1931), on a wide variety of substances, has confirmed this result.

**Gaseous Films of Soluble and Insoluble Substances.** The identity of the ideal equation ( $Fa = kT$ ) applicable to the surface layers of dilute solutions of soluble fatty acids and that deduced for gaseous surface films of insoluble substances (p. 369), as well as the similarity of the deviations from the ideal laws observed in each case, suggests that the difference between these surfaces is purely one of degree, and not kind. This supposition is borne out by the fact that in concentrated solutions of soluble compounds the orientation of the molecules at the surface is the same as in surface films under compression. Further, the surface pressure, or compression, of an oil film as measured by the float method of Langmuir and of Adam is really the difference between the surface tension of pure water ( $\gamma_0$ ) on one side of the floating barrier, and of the water coated with an oil film ( $\gamma$ ) on the other side of the barrier. Hence the surface pressure ( $F$ ) of an insoluble film is equal to  $\gamma_0 - \gamma$ , and this is the same as the definition of  $F$  for the surface layer of a dilute solution of a soluble compound (p. 374). It follows, therefore, that the gaseous films, studied by Adam, and the surface of a dilute solution, studied by Rideal and Schofield, are similar; the same equation  $Fa = kT$  is applicable to ideal cases of both types,  $F$  being defined in each case as the "surface pressure," or  $\gamma_0 - \gamma$ .

Evidence in favour of these ideas is supplied by the fact that there is no discontinuity in the  $Fa-F$  curves in passing from one type of surface to the other. For soluble substances these curves may be obtained by the method of Schofield and Rideal (p. 374) from ordinary surface tension measurements on dilute



solutions ; this has been done for acids containing up to twelve  $\text{CH}_2$  groups. For sparingly soluble substances the  $Fa-F$  curves have been determined by Adam from measurements of the surface pressures of unimolecular films occupying various areas, and for fatty acids these curves have been obtained with compounds containing twelve  $\text{CH}_2$  groups and upwards. If the curves obtained by the two methods are plotted on the same diagram, the whole series shows a gradual transition as the hydrocarbon-chain is lengthened, and there is nothing to indicate that the method of measurement has changed. For the acid containing twelve  $\text{CH}_2$  groups, which has been studied by both methods, the two curves are almost identical. It may be noted in passing that the surface tension method for obtaining the  $Fa-F$  curves involves the use of the Gibbs adsorption equation, whereas Adam's method is one of direct measurement ; the striking agreement between the results obtained by the two methods appears to be good evidence in favour of the fundamental accuracy of the Gibbs equation. Other methods of verifying the relationship involve so many sources of error and assumptions that it is interesting to have this confirmation from a study of surface films.

### THE ADSORPTION OF GASES

The concept of oriented unimolecular layers, already described in connection with oil films on water and with the surfaces of solutions, has been applied by Langmuir (1916) to the study of the adsorption of gases on solid surfaces. The subject is closely connected with the mechanism of heterogeneous catalysis, as well as with the general problems of adsorption, and so merits further consideration. Until about 1916 it had been generally accepted that an adsorbed gas could be regarded as in a "condensed" state on the surface of the adsorbent ; in other words the gas in immediate contact with the solid surface was considered to have a high density, and to become more rarefied further from the surface until the density was the same as in the bulk of the gas. Langmuir, however, replaced this concept of physical adsorption by one involving chemical forces ; his ideas may be expressed as follows.



In the interior of an adsorbent the field of force of each atom is satisfied by the surrounding atoms; the atoms in the surface, however, have a residual field of force, since they are not completely surrounded by other similar atoms. This residual field may result in a sharing of electrons, virtually the same as a covalent linkage, between the surface atoms and an adsorbed gas. Adsorption of this type is now frequently known by the name of "chemisorption," and is, on the whole, of an irreversible nature. If the interaction between the electrical field of the surface and that of adsorbed gas molecules is not so intense as to lead to electron sharing then the adsorption is of the reversible type, now known as "physical" or "Van der Waals" adsorption. Although Langmuir did not distinguish between these two types, his arguments may be taken as applying in general to both.

**Stable Gas Films.** Langmuir obtained evidence in favour of the presence of very stable adsorbed films of gas on the surface of metals; such stability is to be anticipated, in many cases, if the gas is supposed to be held to the surface by chemical forces. At a temperature of  $1900^{\circ}\text{K}$ . a pressure of  $10^{-6}$  atm. of oxygen already had a marked effect in reducing the electron emission from heated tungsten filaments; a film of some kind must be present, having evidently such remarkable stability that it is able to remain on the tungsten in spite of the high temperature and low pressure. The obstructive film, which prevents the electron emission, is quite invisible; it is not the oxide  $\text{WO}_3$ , for although this substance is formed by the interaction of oxygen and tungsten it distils off from the filament at temperatures as low as  $1000^{\circ}\text{K}$ . It can only be concluded, therefore, that oxygen is adsorbed on the tungsten and held much more firmly than would be anticipated if it were merely condensed on the surface. Langmuir has also found that this oxygen film on tungsten not only prevents the dissociation of hydrogen into atoms, which clean tungsten is able to bring about at  $1500^{\circ}\text{K}$ ., but it also does not react with hydrogen; the chemical properties of the oxygen have thus become modified, as might be expected if it is sharing electrons with the tungsten atoms. In the course of time at  $1500^{\circ}\text{K}$ ., however, the oxygen reacts completely with the tungsten



and the resulting trioxide distils off; the clean filament is now able to cause hydrogen molecules to dissociate into atoms. Similar stable films have been observed in other cases, particularly in the chemisorption of oxygen on carbon, but it must be remembered that not all adsorbed gases are attached in such a firm manner.

**Unimolecular Gas Layers.** According to the views generally accepted by physicists the field of force due to atoms does not extend through space to a distance greater than  $2 - 3 \times 10^{-8}$  cm., that is, of the order of a molecular diameter. Hence when a single layer of molecules, or atoms, of a gas has formed on the surface of a solid, the residual field of the latter will be almost completely satisfied. This is similar to the observation that although a unimolecular film of an oil will form on the surface of water, owing to the attraction between the latter and a polar group, the attraction does not extend sufficiently to allow a second layer of molecules to form. As a general rule it may be considered that an adsorbed gas will form only a unimolecular, or monatomic, layer on the surface of a solid. These theoretical considerations, therefore, lead to the conclusion that thick, stable, adsorbed gas films, such as were postulated by many early workers on adsorption and allied subjects, probably do not exist, but that only a unimolecular layer is firmly attached to the adsorbent, and subsequent layers, if any, are held very loosely. This view applies equally to molecules held by chemical or by physical forces.

Direct experimental proof of the presence only of unimolecular gas films in adsorption is difficult to obtain, since surfaces are never ideally smooth and an exact determination of the total area is not possible. Langmuir has studied the adsorption of various gases on smooth surfaces of glass, mica and platinum, and obtained results which bear out the theory of unimolecular layers. It was found that for the gases nitrogen, methane, carbon monoxide, argon, oxygen and carbon dioxide about  $0.6 - 0.7 \times 10^{15}$  molecules were adsorbed per sq. cm. of solid surface; the rough constancy of the value suggests that layers of the same thickness are formed in every case. If the average distance between the atoms in a solid is taken as  $3 \times 10^{-8}$  cm., the area covered by



each is  $9 \times 10^{-16}$  sq. cm., and the number of atoms per sq. cm. is of the order of  $10^{15}$ ; assuming, as Langmuir does, that each atom of metal in the surface attaches to itself one molecule of gas, the formation of a unimolecular layer of any gas would mean the adsorption of approximately  $10^{15}$  molecules per sq. cm. The agreement of this calculated value with those observed by Langmuir is strong evidence for the theory under discussion.

Another argument in favour of the unimolecular film theory is that in many instances the adsorption of a gas by a solid reaches a definite limiting value as the pressure is raised; this is very similar to the limit of adsorption observed in connection with solutions (p. 352) and attributed to the production of a complete unimolecular layer. Owing to the fact, however, that an adsorbing surface is probably never uniform, and that often direct solution, or even slow chemical combination, of the gas in the adsorbing material may occur, the maximum of adsorption is sometimes not observed. Apart from these disturbing factors there seems to be good reason to believe that there is a definite limit of adsorption, provided, however, the adsorbed vapour is not in the vicinity of its saturation pressure; in the latter circumstances it is very probable that condensation will occur on the solid. This phenomenon must be regarded as distinct from that of true adsorption, although there is often confusion between them. In conclusion it may be recalled that very small amounts of suitable poisons are sufficient to inhibit completely the activity of certain catalysts; the quantities adsorbed in this manner are hardly sufficient to produce a film more than one molecule deep, yet this is quite able to reduce the adsorptive power of the surface for other substances to a negligible amount. On the whole it may be stated, therefore, that provided the pressure of a gas is not close to its saturation value, a stable unimolecular film is formed in adsorption. There is some evidence, however, that under suitable conditions a partial second layer, held by van der Waals forces, may exist above the unimolecular film attached firmly by chemisorption (Roberts, 1935). Further, the work of Lambert and Heaven (1936), on the adsorption of mixtures of oxygen and argon by silica gel suggests that there are two layers of gas on the surface,







"elementary spaces," per sq. cm. of adsorbent,  $\eta$  the number of gm. mols. of gas adsorbed per unit surface and  $N$  the Avogadro number, then  $N\eta/N_0$  represents the fraction of the total number of available spaces covered with gas molecules when equilibrium is attained. Hence  $N\eta/N_0$  is equal to  $\theta$ ; substituting in equation (xxxii.) it follows that

$$\eta = \frac{N_0 a \mu}{N(\nu + a \mu)} \quad \dots \quad (xxxiii.)$$

For a given gas and a given solid adsorbent  $N_0$ ,  $a$  and  $\nu$  are constants;  $N$  is a universal constant,  $\mu$ , as already shown, is proportional to the pressure  $p$ , and  $\eta$  is proportional to the mass of gas adsorbed per unit mass of adsorbent; hence

$$\frac{x}{m} = \frac{k_1 k_2 p}{1 + k_1 p} \quad \dots \quad (xxxiv.)$$

where  $x$  is the total mass of gas adsorbed by a mass  $m$  of adsorbent, and  $k_1$  and  $k_2$  are constants for the substances under consideration at a definite temperature. This equation, which is an "adsorption isotherm," may be written in the form

$$\frac{p}{x/m} = \frac{1}{k_1 k_2} + \frac{p}{k_2} \quad \dots \quad (xxxv.)$$

and so the plot of  $p/(x/m)$  against  $p$  should be a straight line; Langmuir and others (*e.g.*, McBain, 1930; Bawn, 1932) have found that this is actually so for many adsorption processes. In the adsorption of carbon monoxide on platinum, however, the results appear to comply with the formula

$$\frac{x}{m} = k + \frac{k_1 k_2 p}{1 + k_1 p} \quad \dots \quad (xxxvi.)$$

The presence of the constant  $k$  may be attributed to the formation of a very stable complete layer of gas, upon which a subsequent unimolecular layer, satisfying the requirements of the Langmuir isotherm (equation (xxxiv.)), is adsorbed. It is not impossible, however, that the deviation from the simple equation may be due to differences in the adsorptive power for carbon monoxide of different parts of the platinum surface. For example, if there are several types of elementary spaces on the adsorbing



material constituting areas which are fractions  $\beta_1, \beta_2, \beta_3$ , etc., of the total available surface, where

$$\beta_1 + \beta_2 + \beta_3 + \dots = 1,$$

then it may be readily shown, by the method already used, that

$$\theta = \frac{\alpha_1 \beta_1 \mu}{\nu_1 + \alpha_1 \mu} + \frac{\alpha_2 \beta_2 \mu}{\nu_2 + \alpha_2 \mu} + \frac{\alpha_3 \beta_3 \mu}{\nu_3 + \alpha_3 \mu} \quad (\text{xxxvii.})$$

$\alpha_1$  and  $\nu_1$  referring to the fraction  $\beta_1$ , and so on. An equation of this type, involving two terms, has been found by Bawn (1932) to apply to the adsorption of argon on mica. If  $\nu_1$  is very small, that is, there is very little tendency for the molecules to evaporate from one particular part of the surface, then the first term on the right-hand side of the equation is almost a constant, and the whole may be reduced to a form similar to that found by Langmuir for carbon monoxide on platinum. There are many lines of evidence (see Chapter VIII.) which point to the fact that the surface of an adsorbent is not uniform, and so this alternative explanation of the equation (xxxvi.) for the adsorption of carbon monoxide is quite reasonable.

Two special cases of the simple adsorption isotherm are of interest: at very low pressures, or for a poor adsorbent, only a small fraction of the surface will be covered with molecules; hence  $\theta$  is small, and  $1 - \theta$  is almost equal to unity. Equation (xxxi.) therefore reduces to

$$a\mu = \nu \theta \quad \dots \dots \dots (\text{xxxviii.})$$

and

$$\frac{x}{m} = k_1 k_2 p \quad \dots \dots \dots (\text{xxxix.})$$

Under these conditions it follows then that the amount of gas adsorbed is directly proportional to the pressure. When the adsorption is great, however,  $\theta$  is almost unity, and equation (xxxi.) may be written

$$(1 - \theta)a\mu = \nu \quad \dots \dots \dots (\text{xl.})$$

$$\therefore \theta = 1 - \frac{\nu}{a\mu} \quad \dots \dots \dots (\text{xli.})$$



From this it follows that

$$\frac{x}{m} = k_2 - \frac{k_2}{k_1 p} \quad \dots \quad \text{(xlii.)}$$

As  $p$  is increased,  $k_2/k_1 p$  becomes gradually smaller, and so  $x/m$  tends towards a limit of  $k_2$ ; the Langmuir isotherm is thus in agreement with many observations of a definite adsorption maximum (p. 381).

## SURFACE MOBILITY OF MOLECULES

In the original Langmuir theory it was tacitly implied that when a gas molecule condensed on to a particular atom of adsorbent it remained there until it evaporated; during the past few years evidence has been accumulating which requires a modification of this view; for it appears reasonably certain that adsorbed molecules are able to move laterally on, that is parallel to, the surface of the adsorbing material.

When studying the growth of a mercury crystal, as a result of condensation from mercury vapour, Volmer and Estermann (1921) found that certain faces of the crystal grew a thousand times as rapidly as they received molecules from the vapour; these molecules must either be able to penetrate the solid crystal or, what is more probable, the molecules adsorbed on other parts of the crystal are able to migrate to the rapidly growing face. In an extension of this work Volmer and Adikhari (1925) allowed a succession of mercury drops to brush against a long crystal of benzophenone; owing to the gradual removal of the latter the crystal wears away, not only at the place where the mercury drops touch but at some distance from it. Clearly the benzophenone molecules are able to move over the surface of the crystal. More striking confirmation of lateral mobility was obtained by an experiment in which a stream of mercury drops brushed against the edge of a glass plate 0.1 to 1 mm. away from some benzophenone deposited on the glass; although the mercury did not come into actual contact with the benzophenone it was worn away because of the movement of the molecules adsorbed on the glass. Similar results were recorded by Moll (1928) for a number of other solids, and for



benzophenone and salol observations under crossed Nicol prisms showed that the crystals were becoming thinner at points where they were not being touched.

Evidence of another type was obtained by Estermann (1923): silver was deposited from a uniform "molecular beam" (see p. 141) on to a glass plate, so that the deposit should have been 1—2 atoms thick; ultramicroscopic examination showed, however, that it was not uniform, and although the atoms of silver must have arrived at a uniform rate over the whole surface actually they were in isolated clusters of about a thousand atoms each. This could only have resulted if the silver atoms were able to migrate laterally over the glass surface, and the same supposition was necessary to explain other observations made by Estermann (1925) with the molecular beam of silver. Similar results concerning the non-uniformity of the deposits were obtained by Cockroft (1928) using a beam of copper atoms; this author found that the introduction of a wire in the way of the beam did not cast a sharp "shadow" on the plate collecting the deposit. The creeping of the copper atoms into the space which should have been shadow could only have been due to their mobility on the glass plate.

Still another aspect of the subject has been indicated by Ward (1981), who found that the heat of adsorption of hydrogen on copper was uniform and did not vary with the amount adsorbed; since the surface of the copper cannot be uniform (see Chapter VIII.) it might be anticipated that different values would be obtained at different stages of adsorption. Actually by baking the copper at  $150^{\circ}$ — $200^{\circ}$  for some hours, so as to cause sintering, the heat of adsorption of hydrogen was decreased, but it was still uniform. The conclusion to be drawn is that the adsorbed molecules move freely over the surface of the copper from atom to atom, and the actual heat measured is the mean value for the surface as a whole. Further, the concept of lateral diffusion of adsorbed molecules on a solid surface has been found to be in harmony with the influence of temperature on the adsorption maximum (Wilkins and Ward, 1929), with the effect of pressure on the oxidation of copper (Wilkins, 1980) and with the expansion











is raised, since adsorption is an exothermic process. As the temperature is increased still further a condition is attained in which the rate of the activated process becomes appreciable and the amount of this type of adsorption, during the time of an experiment, should have the effect of causing an increase in the total adsorption. This increase may continue over a range of temperature until the normal effect of temperature on the amount adsorbed, apart from the rate of adsorption, brings about a decrease.

An examination of published data on adsorption, as well as new observations by Taylor and his co-workers (1931-35), and by others, has revealed strong evidence for the theory of activated adsorption. For example, at  $-78^{\circ}$  the adsorption of hydrogen on a mixture of manganous and chromic oxides is small and rapidly attained; at  $0^{\circ}$  the amount adsorbed is less, but there is evidence of a new type of slow adsorption which becomes measurable over a period of several days. As the temperature is increased the new adsorption becomes more appreciable until at  $305^{\circ}$  the amount of hydrogen adsorbed is fifteen times as great as at  $-78^{\circ}$ , for the same pressure of gas. This increase represents real adsorption and not chemical action with the oxide adsorbent, because nearly the whole of the hydrogen can be recovered by reducing the pressure. At  $440^{\circ}$  the normal decrease in the total amount adsorbed brought about by raising the temperature becomes evident. It seems clear that two entirely different types of adsorption are occurring, and determinations of the heats of adsorption, by applying the van't Hoff isochore to the measured values of the total quantities adsorbed, gave the values as 1,900 cal. from  $-78^{\circ}$  to  $0^{\circ}$ , and 19,000 cal. from  $305^{\circ}$ — $444^{\circ}$ . Direct experimental measurement by Garner (1932) of the heats of adsorption of gases over a range of temperature yielded results of a similar type. The temperature at which activated adsorption is appreciable depends on the substances concerned; it need not necessarily be as high as those mentioned, especially if the energy of activation is not very large. For example, activated adsorption of hydrogen on zinc oxide, promoted with chromium oxide, commences at  $-78^{\circ}$  (Taylor and Sickman, 1932). Not all gases and



adsorbents, however, show activated adsorption, and it is only for the types that do so that the phenomena described here would be anticipated.

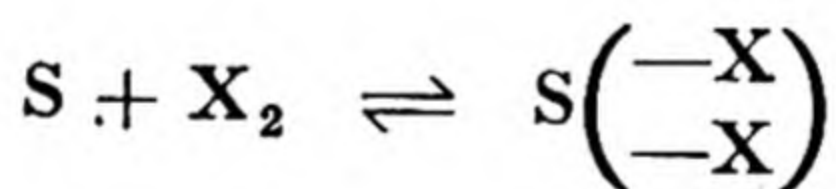
Further investigation has shown that the phenomena of activated adsorption are sometimes complicated: observations on the adsorption of hydrogen on zinc oxide indicate that there are three distinct types of adsorption. The first is a van der Waals adsorption at temperatures up to  $-78^{\circ}$ , then there is a slow process extending from  $0^{\circ}$  to about  $100^{\circ}$  requiring an activation energy of about 5,000 cal., and finally another type of activated adsorption between  $100^{\circ}$  and  $800^{\circ}$ , for which the requisite energy is about 12,000 cal. The presence of chromium oxide as a promoter resulted in a marked increase of the van der Waals adsorption, and now only one type of activated adsorption, commencing at  $-78^{\circ}$ , was observed (Taylor and Strother, 1934). Another aspect of the subject has been opened up by the somewhat unexpected discovery that the rate of activated adsorption of hydrogen was the same as that of deuterium on various oxide surfaces (Pace and Taylor, 1934; Kohlschütter, 1934). This result is incompatible with the view that it is the adsorbed molecule which has to acquire the energy of activation, for if this were the case the difference in zero-point energy would result in a greater rate of adsorption of hydrogen than of deuterium (see "Recent Advances in General Chemistry," Chapter III). As a consequence of further investigation of the effect of pressure on the adsorption of hydrogen on chromium sesquioxide gels, Burwell and Taylor (1936) have suggested that the slow process of adsorption may be ascribed to an interaction between molecules adsorbed by van der Waals forces and parts of the adsorbing surface which acquire the necessary activation energy.

The concept of slow activated adsorption has been criticised by Steacie (1931), Ward (1931), Burrage (1932) and Garner and Veal (1935); apart from experimental weaknesses, the main point made is that the so-called slow adsorption is really a solution effect, the gas penetrating, or diffusing, into the solid adsorbent. This cannot, however, be a complete explanation. Kingman (1932) has noted that the rate of this slow process is proportional



to the pressure of the gas and to the extent of the *free* surface of the solid; if the process were one of dissolution or diffusion the rate might be expected to be proportional to the area of the surface *covered* with adsorbed gas. Further, Garner (1932) has pointed out the high temperature coefficient of the activated adsorption shows that it cannot be due to diffusion, which would normally increase in direct proportion to the square root of the absolute temperature. The fact that the high-temperature, slow adsorption of hydrogen on chromium sesquioxide gel diminishes the van der Waals adsorption suggests that the former is a surface process, and cannot be accounted for by slow penetration into the interior of the solid (Howard, 1933). Evidence of a similar nature has been obtained by Emmett and Harkness (1935), which shows that the so-called activated adsorption must be, at least in part, a surface phenomenon.

The suggestion has been made that the cause of the distinction between general and activated adsorption is that, whereas the former is due to physical forces, the latter involves forces of a chemical nature. For example, Taylor considers that in the activated adsorption of hydrogen the gas is really adsorbed in the atomic form, thus



where S refers to the surface and  $X_2$  to the adsorbed molecule. The hydrogen atoms presumably remain attached to the surface atoms by chemical forces such as those postulated by Langmuir; in fact Benton (1932) states that the only difference between this type of adsorption and chemical combination is that the adsorbent atoms form part of the crystal lattice and no new phase is formed. Garner (1935) prefers to regard all cases of so-called activated adsorption as types of "chemisorption," since there is no real evidence that it is the adsorption process which requires the activation energy, whereas there is good reason to believe that in many cases chemical interaction of some kind is involved. Reference to the connection between activated adsorption and certain aspects of catalysis will be made in the next chapter.



## REFERENCES

- ADAM *et al.* *Proc. Roy. Soc.*, 1921, 99A, 336 ; 1922, 101A, 452, 516 ; 1923, 103A, 676, 687 ; 1924, 106A, 694 ; 1926, 110A, 423 ; 112A, 362, 376 ; 1928, 117A, 532 ; 119A, 628 ; 120A, 473 ; 1930, 126A, 526 ; 1932, 138A, 411 ; 1933, 142A, 401, 416 ; 143A, 104 ; 1935, 147A, 491 ; *Trans. Faraday Soc.*, 1928, 24, 150 ; *Science Progress*, 1927, 21, 431\*, 621\* ; *Chem. Reviews*, 1926, 3, 184\* ; *Koll. Z.*, 1931, 57, 188\* ; "Physics and Chemistry of Surfaces," 1930\*.
- ALLMAND *et al.* *Proc. Roy. Soc.*, 1930, 129A, 235, 252 ; 1931, 130A, 197, 210, 610 ; 132A, 460 ; 1932, 134A, 554 ; *Trans. Faraday Soc.*, 1932, 28, 218, 223 ; *J. Physical Chem.*, 1931, 35, 1692.
- BANGHAM and FAKHOURY. *J. Chem. Soc.*, 1931, 1324.
- BARTELL and MACK. *J. Physical Chem.*, 1932, 36, 65.
- BAWN. *J. Amer. Chem. Soc.*, 1932, 54, 72.
- BRADLEY. *Phil. Mag.*, 1929, 8, 202 ; 1931, 11, 690 ; *Chem. Reviews*, 1931, 9, 47\*.
- BURRAGE. *J. Physical Chem.*, 1930, 34, 2202 ; 1933, 37, 41.
- BUTLER *et al.* *J. Chem. Soc.*, 1932, 2089 ; 1934, 528.
- Discussion on "The Adsorption of Gases by Solids," *Trans. Faraday Soc.*, 1932, 28, 131\*.
- EMMETT and HARKNESS. *J. Amer. Chem. Soc.*, 1935, 1624, 1631.
- GARNER. *Trans. Faraday Soc.*, 1932, 28, 261 ; *J. Chem. Soc.*, 1935, 1487.
- GREGG. "The Adsorption of Gases by Solids," 1935\*.
- GUGGENHEIM and ADAM. *Proc. Roy. Soc.*, 1932, 139A, 218.
- HARKINS *et al.* *J. Amer. Chem. Soc.*, 1917, 39, 354, 541 ; 1919, 41, 970 ; 1920, 42, 700, 2537 ; 1921, 43, 35 ; 1930, 52, 2289 ; 1931, 53, 850 ; 1935, 57, 2224 ; *J. Chem. Physics*, 1933, 1, 852 ; 1935, 3, 692.
- HOWARD. *Trans. Faraday Soc.*, 1934, 30, 278.
- HÜCKEL. "Adsorption und Kapillarkondensation," 1928\*.
- KAR and GANGULI. *Physikal. Z.*, 1929, 30, 918.
- KINGMAN. *Trans. Faraday Soc.*, 1932, 28, 269.
- KOSAKEWITSCH and USCHAKOWA. *Z. physikal. Chem.*, 1931, 157, 188.
- LAMBERT and HEAVEN. *Proc. Roy. Soc.*, 1936, 153A, 584.
- LANGMUIR. *J. Amer. Chem. Soc.*, 1916, 38, 2221 ; 1917, 39, 848 ; 1918, 40, 1361 ; *Third Colloid Symposium Monograph*, 1925, 48 ; *J. Chem. Physics*, 1933, 1, 756 ; *Chem. Reviews*, 1933, 13, 147\*.
- LONDON. *Z. physikal. Chem.*, 1930, B11, 222.
- McBAIN. "The Sorption of Gases by Solids," 1932\*.
- McBAIN and BRITTON. *J. Amer. Chem. Soc.*, 1930, 52, 2198.
- MARCELIN. *Ann. Physique*, 1925, 4, 460 ; *Kolloidchem. Beih.*, 1933, 38, 177\*.
- MAXTED. *Ann. Reports*, 1935, 32, 109\*.
- POLANYI. *Z. Elektrochem.*, 1929, 35, 431.
- RIDEAL. *Koll. Z.*, 1932, 61, 177 ; "An Introduction to Surface Chemistry," 1930\*.
- SCHOFIELD and RIDEAL. *Proc. Roy. Soc.*, 1925, 109A, 57 ; 1926, 110A, 167 ; *Phil. Mag.*, 1932, 14, 203.
- SCHULMAN and HUGHES. *Proc. Roy. Soc.*, 1932, 138A, 430.
- STEACIE. *J. Physical Chem.*, 1931, 35, 2112.
- TAYLOR *et al.* *J. Amer. Chem. Soc.*, 1931, 53, 578, 2168, 3604 ; 1932, 54, 602 ; 1934, 56, 586, 2254, 2259 ; *Chem. Reviews*, 1931, 9, 1\* ; *Trans. Faraday Soc.*, 1932, 28, 131.
- VOLMER *et al.* *Z. Physik.*, 1921, 7, 5 ; 1925, 35, 170 ; *Z. physikal. Chem.*, 1922, 102, 267 ; 1925, 115, 253 ; 1926, 119, 46 ; *Trans. Faraday Soc.*, 1932, 28, 359\*.



- WARD. *Proc. Roy. Soc.*, 1931, 133A, 506, 522.  
WILKINS. *Ibid.*, 1930, 128A, 407 ; *Phil. Mag.*, 1931, 11, 690.  
WILKINS and WARD. *Z. physikal. Chem.*, 1929, 144, 259.  
WYNNE-JONES. *Phil. Mag.*, 1931, 12, 907 ; 1932, 14, 203.  
ZEISE. *Z. physikal. Chem.*, 1928, 136, 385.

\* Review papers and books, wherein further references are to be found, are marked by an asterisk.



## CHAPTER VIII

### HETEROGENEOUS CATALYSIS

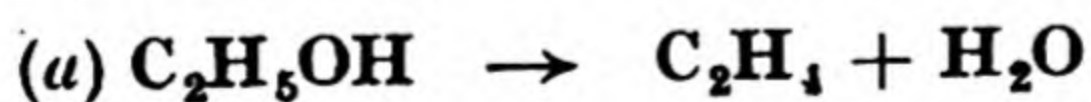
**Adsorption and Catalysis.** For many years it has been realised (*e.g.*, Bone and Wheeler, 1906; Taylor and Burns, 1921) that adsorption plays an important part in heterogeneous catalysis involving gaseous reactants and solid catalysts. The most obvious explanation of the mechanism of such reactions is that the catalyst adsorbs one of the reacting gases, and as a result of the concentration of the latter in a closely packed layer, the probability of impact with other reacting molecules is much greater than if both reactants remained in the gas phase. If a certain proportion of impacts always leads to chemical reaction (Chapter V.), it is clear from the point of view outlined that the rate of reaction should be greater in the presence of a suitable catalyst. This simple theory, however, cannot by any means cover the facts concerning heterogeneous gas reactions. It will be shown later that as a general rule catalytic reactions involving two gases, for example, occur when *both* types of molecules are adsorbed by the catalyst; in fact there are very few cases in which it can be definitely established that reaction occurs as a result of the impact of molecules from the gas phase with those in the adsorbed layer. Another objection to the simple concentration hypothesis is that a number of different catalysts might be expected to have the same effect on a given reaction; if each catalyst, as is not improbable, adsorbed a complete unimolecular layer of one of the reactants the rate of reaction would depend only on the pressure of the other reactant, and so would be independent of the catalyst.

A further argument against the simple theory proposed is that many heterogeneous reactions involving a single compound, *e.g.*, the decomposition of phosphine, are found to be kinetically unimolecular; that is, the velocity of the reaction is proportional to the pressure of the gas, even down to very low pressures. It is



true that, if the catalytic surface were covered with a complete layer of reactant molecules, and reaction depended on an impact by a molecule from the gas phase, the rate would be proportional to the pressure of the latter. The process would then appear to be unimolecular, although actually it involved a reaction between two molecules, one adsorbed and one free. At very low pressures, however, the adsorbed layer would not be complete; the area covered by reacting gas would be roughly proportional to the pressure of the gas (p. 384), and since the number of molecules striking the surface is also proportional to the pressure, the number of impacts leading to chemical reaction would be dependent on the square of the pressure. The reaction would then be kinetically bimolecular at low pressures; this is actually the case for the decomposition of acetaldehyde at about  $850^{\circ}\text{C}$ . on platinum, gold and tungsten (Hinshelwood and Allen, 1928), and the reaction probably occurs as the result of impacts (p. 407). In the majority of unimolecular heterogeneous reactions, however, the order remains constant at low pressures, and at high pressures the reaction often becomes one of zero order, that is, the rate is independent of the pressure. Such reactions can only involve one molecule in each act of chemical transformation, and there is no possibility of an impact representing the mechanism of the process.

Hinshelwood has emphasised the following point as contrary to the simple impact mechanism: many heterogeneous catalytic reactions involve changes which can occur in two different ways. For example, ethyl alcohol vapour may be decomposed either into (a) ethylene and water, or (b) acetaldehyde and hydrogen, thus



or



At different surfaces the concentration of alcohol molecules might possibly be different, but since the rate of reaction is proportional to the pressure of the alcohol vapour, it would be anticipated, from the impact theory, that the two reactions will be affected to the same extent by a change of catalyst. That is, although the total amount of alcohol decomposed might be different with different catalysts, the proportions involved in the two possible reactions •



should remain almost unchanged. This is certainly not the case : with copper as catalyst at  $300^{\circ}\text{C}$ . the decomposition is almost entirely into aldehyde, whereas alumina at the same temperature favours the reaction yielding ethylene. Other examples of this type of behaviour are known, *e.g.*, the decomposition of formic acid vapour, and the conclusion must be drawn that there is some specific relationship between the catalyst and the adsorbed reactant. The first explanation which suggests itself is that the catalyst causes the adsorbed molecules to orient themselves in a definite manner ; one catalyst, causing one type of adsorption, will favour one reaction, whereas another catalyst to which the reacting molecules are attached in a somewhat different manner will favour the alternative reaction. Whatever the mechanism, however, it is clear that the catalyst has a more direct influence in the reaction than that of acting merely as a surface upon which the reacting molecules may be concentrated.

**The Complexity of Catalysed Reactions.** Catalysed reactions are often more complex than would appear upon a cursory examination ; for example, Bodenstein and Fink (1907) found that the rate of formation of sulphur trioxide in the combination of sulphur dioxide and oxygen on a platinum surface was directly proportional to the sulphur dioxide, or to the oxygen, concentration when the other gas was present in excess, but inversely proportional to the square root of the concentration of sulphur trioxide. It is clear that the presence of the latter is retarding the catalytic action ; other examples of this type of retardation are quite common in heterogeneous reactions, and will be discussed in the course of the present chapter. In order to account for these phenomena Bodenstein assumed that the reacting molecules must diffuse through a layer of the retarding gas, *e.g.*, sulphur trioxide, before they could reach the catalyst, and that the actual rate of reaction at the surface was great in comparison with the rate of diffusion to it. The rate of reaction should thus be dependent only on the rate of diffusion of oxygen through the layer of sulphur trioxide, and would consequently be proportional to the oxygen concentration and inversely to some power—actually one-half—of the concentration of trioxide.



The diffusion theory of retardation, however, meets many difficulties. In the first place the increased rate of a catalysed reaction with increasing temperature would be expected to be due to the increased rate of diffusion of the reacting gases through the retarding layer; the rate of gaseous diffusion increases as the square root of the absolute temperature, but reaction velocities increase very much more rapidly than this as the temperature is raised. Secondly, Langmuir has pointed out that the theory requires the existence of films relatively thick in proportion to the dimensions of a molecule, since it is found that reaction velocities of the type under discussion can vary a thousand-, if not a million-, fold. In such cases it would be necessary to postulate films so thick as to be visible to the eye! Actually it has been found that the amount of sulphur trioxide adsorbed by platinum is of the order required to form a single molecular layer; it appears, therefore, difficult to accept the view that the thickness of the film varies very considerably with changes of pressure. An alternative concept of the action of retarding gases has been proposed by Langmuir, and will be described shortly; it is based on the same fundamental principles as is his theory of adsorption discussed in the previous chapter, and gives a much more acceptable picture of catalytic action and retardation than does the diffusion theory.

### MECHANISM OF CATALYTIC REACTIONS

In rejecting the older theories of catalysis it is necessary to seek for new view-points, and in this connection it seems advisable to examine the subject from two different aspects: it is necessary, firstly, to discover why adsorbed molecules, apart from the question of concentration, are in a particularly reactive state, and, secondly, to determine the mechanism of the actual reaction in any particular case. The latter aspect of the problem will be discussed first, as in this matter the views of Langmuir have proved to be very illuminating. Although these views have undergone some modification, owing to the possibility of lateral motion of adsorbed molecules in a catalyst surface (p. 385), their application in con-







where  $\nu_2$  determines the rate of evaporation of the molecules of *resultant*. Substituting the value for  $\theta$  obtained from equation (i.) in this, it follows that

$$\frac{dx}{dt} = \nu_2 \left( \frac{\alpha \mu}{\nu_1} \right)^{m/n} \dots \dots \dots (iii.)$$

Since  $\nu_1$ ,  $\nu_2$  and  $\alpha$  are constants, and  $\mu$  is proportional to the pressure of the gas (p. 382),

$$\frac{dx}{dt} = kp^{m/n}; \dots \dots \dots (iv.)$$

that is, the velocity of reaction is proportional to the  $m/n^{\text{th}}$  power of the gas pressure. In the dissociation of hydrogen on a tungsten filament Langmuir found that the rate was proportional to the square root of the hydrogen pressure, and so  $m/n$  is equal to 0.5. It appears, therefore, that the hydrogen molecule occupies two elementary spaces ( $n = 2$ ) on the tungsten surface, and the resulting hydrogen atoms each come from one of these spaces ( $m = 1$ ). In the reverse reaction, namely the combination of hydrogen atoms on tungsten, it was found that  $m/n$  was equal to 2; hence  $m = 2$  and  $n = 1$ , and it may be concluded that two adjacent hydrogen atoms, each occupying one elementary space, unite to form a molecule.

**Order of Catalytic Reactions.** The order of a chemical reaction involving a single reacting species is generally determined by the fact that the rate of reaction is proportional to the  $z^{\text{th}}$  power of the pressure, or concentration, where  $z$  is the number of reacting molecules concerned in each act of chemical transformation; this relationship may be expressed by the equation

$$\frac{dx}{dt} = kp^z \dots \dots \dots (v.)$$

Alternatively the order of the reaction may be determined by the application of the well-known fact that the time taken to decompose half of the original amount of the reacting substance is inversely proportional to the  $z - 1^{\text{th}}$  power of the initial pressure, or concentration, ( $a$ ); thus

$$\tau = \frac{1}{ka^{z-1}} \dots \dots \dots (vi.)$$

where  $\tau$  is the time of half-change.



Consider the dissociation of hydrogen on tungsten : as already indicated

$$\frac{dx}{dt} = kp^{0.5},$$

and so the apparent order of reaction is one-half ! The actual reaction is, however, unimolecular ; the fraction 0.5 appears because the molecule condenses on two elementary spaces of the catalyst. This is one illustration—more will be given shortly—of the danger of inferring the number of molecules taking part in a *heterogeneous* reaction, that is the true order, from the relationship between the reaction velocity and the pressure of the gas.

For many catalytic reactions involving a single gaseous compound it has been found that  $m/n$  is equal to unity, and the reactions appear to be unimolecular, with  $m = n = 1$ . Examples of this type are the decomposition of arsine, phosphine and formic acid on various surfaces, nitrous oxide on gold, and hydrogen iodide on platinum. In these cases it is possible that  $m = n = 2$ , when  $m/n$  is still equal to unity ; this would imply that each adsorbed molecule occupied two elementary spaces of the catalyst, and that the occupants of two adjacent spaces were involved in the decomposition. This is exactly the same as saying that one molecule only is involved in each act of transformation, and so the reactions may for the present be regarded as strictly unimolecular.

**Reactions of Variable Order.** The decomposition of ammonia on molybdenum or tungsten appears to be unimolecular at low pressures, but as the initial pressure of the gas is increased the rate of decomposition becomes constant and independent of the pressure ; the reaction, therefore, changes from the first order to one of zero order. This type of behaviour is not uncommon, and can be readily accounted for by the fact that at high pressures the layer of gas molecules on the catalyst becomes complete. When the surface is saturated the number of molecules on the surface, and hence the rate of reaction, is independent of the pressure. The same conclusion may be reached by putting  $\theta$ , which represents the area of the covered surface, in equation (ii.) as equal to unity ;  $dx/dt$  is then found to be a constant under these conditions. Since a reaction, although really unimolecular, may



become of zero order as the pressure increases, it is clearly important to study the reaction velocity at various pressures before deciding on its true order. At pressures intermediate between those at which the reaction is of the first and apparently of zero order, that is when the surface is covered to an appreciable extent but not completely, the order of the reaction appears to be fractional. If  $\theta$ , as before, is the fraction of the available surface which is covered, then

rate of condensation of reacting gas  $= a\mu(1 - \theta)$ .

For a unimolecular reaction  $m$  and  $n$  may be assumed to be unity, and so it is possible to write

$$\text{rate of evaporation of reacting gas} = \nu_1 \theta.$$

For equilibrium the rates of condensation and evaporation are equal, and so

$$a\mu(1 - \theta) = v_1\theta \quad . \quad . \quad . \quad . \quad . \quad (\text{vii.})$$

$$\therefore \theta = \frac{a\mu}{a\mu + \nu_1} \quad \dots \dots \dots \text{(viii.)}$$

The rate of reaction is given by

[illegible]

where  $\nu_2$ , as previously, represents the rate of evaporation of the resultant molecules ; substituting the value for  $\theta$  from equation (viii.), then

$$\frac{dx}{dt} = \frac{\nu_2 \alpha \mu}{\alpha \mu + \nu_1} \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot (\text{x.})$$

$$= \frac{k_1 p}{k_2 p + 1} \cdot \cdot \cdot \cdot \cdot \cdot \cdot \quad (\text{x.a})$$

From this equation it may be seen that the rate of reaction is rather less than would be required by direct proportionality between  $dx/dt$  and  $p$ , as should be the case for a first order reaction ; such a relationship may also be expressed approximately in the form

[illegible]



where  $c$  is less than unity. For the decomposition of stibine on a surface of metallic antimony at  $25^{\circ}\text{C}$ ., Bodenstein and Stock (1907-8) found that the rate of reaction was proportional to  $p^{0.6}$ . By analogy with arsine, phosphine and ammonia, however, it is very probable that stibine actually decomposes in a unimolecular manner, and the value of the apparent order of 0.6 must be due to the fact that the surface is covered with stibine molecules to an appreciable extent, but not completely. At higher temperatures the rate of evaporation of the molecules is increased and the surface becomes more sparsely covered, and eventually the conditions of equation (i.) are operative; the rate of reaction should then become directly proportional to the pressure. In agreement with this view it is found that as the temperature of decomposition of stibine is raised the value of  $c$  in equation (xi.) increases towards unity, and the reaction becomes unimolecular.

The thermal decomposition of germane ( $\text{GeH}_4$ ) on a germanium surface has been studied by Hogness and Johnson (1932), who found that the rate was proportional to the cube root of the pressure over a considerable range of temperature. This result may most readily be explained by making the highly probable assumption that a molecule of germane occupies three elementary spaces on the surface and that the decomposition is unimolecular. Under these conditions equation (vii.) may be written in the form

$$\alpha\mu(1 - \theta)^3 = \nu_1\theta^3 \quad \dots \dots \dots \text{(vii.a)}$$

whereas equation (ix.) remains as before. If the proportion of the surface covered by gases is small, and  $1 - \theta$  may be put as approximately equal to unity, then it follows, since  $\mu$  is proportional to the pressure ( $p$ ) of the germane, that

$$\frac{dx}{dt} = k\sqrt[3]{p} \quad \dots \dots \dots \text{(xii.)}$$

At low temperatures hydrogen acts as a partial inhibitor (*vide infra*) and the velocity deviates somewhat from this relationship.

**Adsorption of Reaction Products.** This type of deviation from the normal order of a reaction occurs when one or more of the reaction products are adsorbed strongly by the catalyst, so that they occupy an appreciable fraction of the surface. During the



course of the reaction the accumulation of the products causes a steady diminution in the fraction of the surface available for the reactant, and so the rate at which it is transformed is reduced below the value expected from the true order of the reaction. In order to obtain an idea of the extent of this diminution a special case will be considered, namely, when the reacting gas occupies only a small fraction of the available surface ; this condition is particularly applicable at low pressures. If  $\theta$  represents the fraction of surface covered, mainly by the *products* of the reaction, then it follows, in accordance with previous deductions, that for equilibrium between the adsorbed layer of the product and its molecules in the surrounding gas

$$a_1\mu_1(1 - \theta) = v_1\theta \quad . \quad . \quad . \quad . \quad . \quad . \quad (\text{xiii.})$$

$$\therefore 1 - \theta = \frac{\nu_1}{a_1 \mu_1 + \nu_1} \quad . \quad . \quad . \quad . \quad (\text{xiv.})$$

where  $\mu_1$  is proportional to the pressure of the product which is supposed to occupy one elementary space per molecule. The rate of reaction is proportional to the rate at which reactant molecules strike the bare parts of the available surface ; hence

$$\frac{dx}{dt} = k_{\mu}(1 - \theta) \quad . \quad . \quad . \quad . \quad . \quad . \quad (\text{xv.})$$

$$= \frac{k_{\mu\nu_1}}{a_1\mu_1 + \nu_1} = \frac{k_1 p}{k_2 p_1 + 1} \dots \dots \dots (\text{xvi.})$$

where  $p$  is the pressure of the reactant, and  $p_1$  that of the adsorbed product, at any instant. The factor  $1/(k_2 p_1 + 1)$  is a measure of the retarding effect of the adsorbed products on the reaction velocity, which would otherwise have been directly proportional to the pressure  $p$ . If the product is strongly adsorbed, that is  $\nu_1$  is small,  $k_2$  which is proportional to  $1/\nu_1$  is large, and  $k_2 p_1$  is great in comparison with unity. The reaction velocity expression under these conditions reduces to

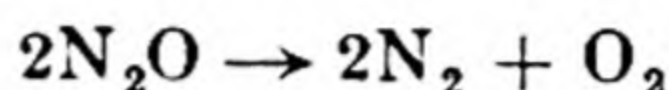
$$\frac{dx}{dt} = \frac{k_1 p}{k_2 p_1} = k \frac{p}{p_1}; \quad \dots \quad \text{(xvii.)}$$

that is, the reaction velocity is directly proportional to the concentration (or pressure) of the reacting substance, and inversely



proportional to that of the retarding product. If the product is not adsorbed to any appreciable extent,  $\nu_1$  is large and  $k_2$  very small; the equation then becomes identical with that for an ordinary unimolecular reaction with no retardation.

**Decomposition of Nitrous Oxide.** When studying the decomposition of nitrous oxide



on the surface of platinum at about  $1000^\circ\text{C}$ . Hinshelwood and Prichard (1925) noted that the time for a given fraction (*e.g.*, 0.5) to be decomposed, increased with increasing pressure. For a unimolecular reaction this fraction should have been independent of the pressure, and for a bimolecular reaction it should have been inversely proportional to the pressure (p. 399); hence it appeared as if the decomposition of nitrous oxide on platinum was a reaction of zero order. Further investigations, however, showed that oxygen, one of the products of the reaction, had a marked retarding influence, presumably because it was adsorbed on the surface and so acted as a catalytic poison. The velocity of decomposition of nitrous oxide should then be given by the equation (cf. equation (xvi.) )

$$-\frac{d[\text{N}_2\text{O}]}{dt} = \frac{k_1[\text{N}_2\text{O}]}{k_2[\text{O}_2] + 1} \quad \dots \quad \text{(xvi.a)}$$

if the actual reaction is really unimolecular. If  $a$  is the original concentration (or pressure) of nitrous oxide, and  $x$  the amount decomposed after time  $t$ , then provided the oxygen present is due only to the decomposition of the nitrous oxide,

$$\frac{dx}{dt} = \frac{k_1(a - x)}{k_2x + 1} \quad \dots \quad \text{(xvi.b)}$$

On integration it follows that

$$k_1 = \frac{1 + ak_2}{t} \ln \frac{a}{a - x} - k_2 \frac{x}{t} \quad \dots \quad \text{(xviii.)}$$

Hinshelwood's measurements are in good agreement with this equation, and so indicate that the catalytic decomposition of nitrous oxide is really a reaction of the first order, but that







the case with hydrogen on platinum, the velocity of a first order reaction is given by the equation (xvii.)

$$\frac{dx}{dt} = \frac{k_1 p}{k_2 p_1} ; \quad \dots \quad \text{(xvii.)}$$

in the case under discussion this becomes

$$\frac{d[\text{NH}_3]}{dt} = \frac{k[\text{NH}_3]}{[\text{H}_2]} \quad \dots \quad \text{(xvii.a)}$$

The observations of Hinshelwood and Burk (1925) that the reaction velocity is inversely proportional to the pressure of added hydrogen is in harmony with this equation. The decomposition of ammonia on platinum gauze at  $772^\circ$ — $858^\circ$  or on copper at  $495^\circ$ — $620^\circ$  also complies with this relationship (Dixon, 1931).

If  $a$  represents the original concentration (or pressure) of ammonia, and  $x$  the amount decomposed in time  $t$ , the velocity equation becomes

$$\frac{dx}{dt} = \frac{k(a - x)}{x} \quad \dots \quad \text{(xvii.b)}$$

and on integration it follows that

$$k = \frac{a}{t} \ln \frac{a}{a - x} - \frac{x}{t} \quad \dots \quad \text{(xx.)}$$

The time of half decomposition,  $\tau$ , is given by

$$\tau = \frac{a}{k} \left( \ln 2 - \frac{1}{2} \right) ; \quad \dots \quad \text{(xxi.)}$$

hence  $\tau$  should be directly proportional to the initial pressure, as is actually found to be the case. This example shows clearly that a reaction which is actually of the first order may become *apparently* of zero order, as a result of strong adsorption of one of the reaction products. It may be noted that the decomposition of phosphine on a molybdenum surface is kinetically unimolecular at low pressures, but becomes of zero order as the pressure is increased and the adsorption of hydrogen presumably becomes important (Melville and Roxburgh, 1938).

**Decomposition of Nitric Oxide.** If a reaction which is really bimolecular is retarded in the manner described, it can be shown



that if adsorption of the product is considerable the velocity equation may be written

$$\frac{dx}{dt} = k \frac{(a-x)^2}{x} \quad \dots \dots \dots (\text{xxii.})$$

and so

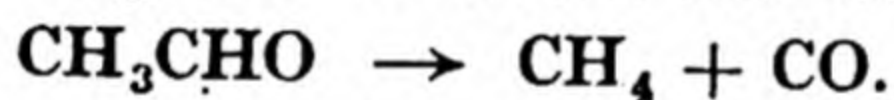
$$k = \frac{1}{t} \left( \frac{x}{a-x} - \ln \frac{a}{a-x} \right) \quad \dots \dots \dots (\text{xxiii.})$$

The period of half decomposition  $\tau$  is then found to be

$$\tau = \frac{1}{k} (1 - \ln 2); \quad \dots \dots \dots (\text{xxiv.})$$

that is  $\tau$  is independent of the initial pressure, and the reaction is *apparently* unimolecular. An example of this type, the decomposition of nitric oxide at heated platinum, has been studied by Hinshelwood and Green (1926) and by Bachmann and Taylor (1929). This reaction is actually bimolecular, but owing to the retardation by very strongly adsorbed oxygen it appears to be unimolecular.

**Decomposition of Acetaldehyde.** An interesting reaction, which has been made the subject of recent study, is the decomposition of acetaldehyde vapour on various catalysts—platinum, platinum-rhodium, gold and tungsten—at about  $850^\circ \text{C}$  :



This reaction is approximately bimolecular for initial pressures below 150 mm. of mercury, but at higher pressures it becomes *apparently* unimolecular (Hinshelwood and Allen, 1928). Three explanations for this type of behaviour are possible. (1) Marked adsorption of one of the products of the reaction at the higher pressures would have the effect observed. If this poisoning occurred, the velocity constant should decrease progressively during the course of the reaction; hence the ratio of  $t_{75}/t_{50}$ , where  $t_{75}$  and  $t_{50}$  represent the times taken to decompose three-quarters and one-half, respectively, of the reacting substance, should be larger than the normal value. (For a bimolecular reaction  $t_{75}/t_{50}$  is equal to 8, and to 2 for a unimolecular reaction.) If the reaction under discussion was being retarded by poisoning of the catalyst, the value of  $t_{75}/t_{50}$  would be greater than 8. Actually it is always between 2 and 8, and so adsorption of a reaction product cannot



be the cause of the change in the apparent order of the reaction. This has been confirmed by the addition of methane and carbon monoxide ; no retarding effect was observed.

(2) If the surface became saturated with acetaldehyde molecules as the pressure was raised, the reaction would become one of apparently zero order, the rate of decomposition being independent of the pressure irrespective of what is really the true order of the reaction. In between the sparsely covered (order = 2) and the completely covered (order = 0) surface the order would be unity ; this, however, would only represent a transition stage. In the actual experiments the order of reaction was found to be unity over a wide range of pressures, with no indication of becoming zero at still higher pressures ; this explanation is, therefore, not tenable.

(8) If the reaction occurred when a molecule from the gas phase struck a molecule adsorbed on the surface, then the reaction velocity would be proportional to the number of molecules per unit surface and to the number of impacts in unit time. The latter is always proportional to the gas pressure, but the former is proportional to this pressure for low values, and independent of the pressure for high values when the surface is saturated. At low pressures, therefore, the reaction rate will be proportional to the square of the pressure, and the reaction is bimolecular ; at higher pressures the velocity is directly proportional to the pressure, and the order is apparently unity. This explanation fits the facts, but it involves the assumption that an impact is involved in the reaction mechanism ; as already indicated, the theory that impact is the cause of reaction is simple and attractive, but the generally accepted opinion is that it is not a satisfactory hypothesis. In the decomposition of acetaldehyde the evidence for impacts resulting in chemical reaction seems to be quite clear, and so the general idea cannot be ruled out in all cases.

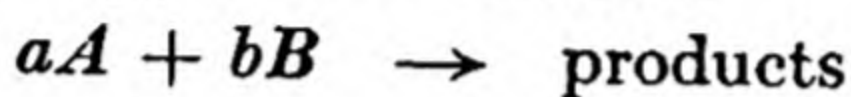
## TWO REACTING GASES

The extension of the theoretical treatment already described to the case of reactions involving more than one reacting gas is somewhat complicated. With two reactants either or both



may be adsorbed to a slight extent, or the surface may be saturated by one of them; further, the catalyst may be poisoned by the strong preferential adsorption of the products of the reaction. In addition, when two different molecules are involved in each act of chemical transformation, the possibility of impacts having an important influence is much greater than when a single reactant only is concerned; this type of mechanism must consequently be considered in addition to the other possibility involving combination between molecules adsorbed on adjacent spaces.

In the first place, suppose the reaction



is occurring on the surface of a catalyst which is only sparsely covered with both of the reactants; further, assume that combination can only occur between molecules of  $A$  and  $B$  adsorbed on adjacent spaces of the surface. If each molecule of the gases  $A$  and  $B$  occupies  $n_1$  and  $n_2$  elementary spaces, respectively, of the surface, then when the sparsely covered adsorbed layer is in equilibrium with the surrounding gases,

$$a_1 \mu_1 = \nu_1 \theta_1^{n_1} \text{ for the gas } A \quad . \quad . \quad . \quad (\text{xxv.a})$$

$$a_2 \mu_2 = \nu_2 \theta_2^{n_1} \text{ for the gas } B \quad . \quad . \quad . \quad (\text{xxv}.b)$$

(see equation (i.), p. 398), where  $\theta_1$  and  $\theta_2$  are the fractions of the surface covered by  $A$  and  $B$  respectively. Suppose reaction occurs between  $A$  adsorbed on  $x$  spaces and  $B$  on  $y$  adjacent spaces, the rate of reaction is given by

$$\frac{dx}{dt} = k\theta_1^x \theta_2^y \quad . \quad . \quad . \quad . \quad . \quad . \quad (\text{xxvi.})$$

where  $x/n_1$  and  $y/n_2$  are equal to  $a$  and  $b$  respectively, that is the number of molecules of  $A$  and  $B$  involved in each act of chemical change. Substituting the values for  $\theta_1$  and  $\theta_2$  obtained from equations (xxv.  $a$  and  $b$ ) in the reaction velocity equation, and putting  $\mu$  proportional to the pressure  $p$  of each gas, it follows that

$$\frac{dx}{dt} = K p_A^a p_B^b \dots \dots \dots (xxvii.)$$

where  $p_A$  and  $p_B$  represent the pressures of  $A$  and  $B$  respectively. This is the simplest type of heterogeneous reaction involving two



substances, but unfortunately there are not many definite instances in which the mechanism is so straightforward. For the combination of carbon monoxide and oxygen on crystalline quartz, Bodenstein and Ohlmer (1905) found that

$$\frac{dx}{dt} = K[\text{CO}] [\text{O}_2]^{\frac{1}{2}}$$

which is in accordance with the requirements of the simple mechanism for the reaction



It is doubtful, however, if the reaction is really as simple as this agreement implies; on quartz glass the rate of combination of carbon monoxide and oxygen was found by Bodenstein to vary as  $[\text{O}_2]/[\text{CO}]$ , but Benton and Williams (1926) found it to be proportional to  $[\text{O}_2] [\text{CO}]^{\frac{1}{2}}$ . This difference may be due to differences in the adsorptive power of the quartz glass, but it certainly implies a rather complex mechanism for the reaction.

**The Ethylene-Hydrogen Reaction.** Pease (1923) found that at temperatures between  $150^\circ$  and  $250^\circ$  C., the rate of combination of ethylene and hydrogen on the surface of copper was approximately proportional to the pressure of each gas. At these elevated temperatures neither gas is adsorbed to any marked extent, and the reaction mechanism is comparatively simple; combination presumably occurs between ethylene and hydrogen molecules adsorbed on adjacent spaces of the catalytic surface. At lower temperatures ( $0^\circ$  to  $20^\circ$  C.) the reaction instead of being bimolecular, appears to be more nearly unimolecular; the velocity under these conditions is approximately proportional to the hydrogen pressure. The explanation of this change is that ethylene is now preferentially adsorbed, and the area it covers is almost independent of its pressure; assuming the same reaction mechanism as already suggested, the rate will depend only on the pressure of hydrogen, which determines the number of molecules striking the portions of the surface adjacent to the adsorbed ethylene. The greater the pressure of the latter gas, the less will be the surface available for hydrogen molecules to condense upon, and so the reaction rate should be reduced. Actually excess of ethylene is



found to inhibit the reaction to some extent ; this inhibiting effect of reactants adsorbed preferentially will be discussed in the next sections.

**Preferential Adsorption of Reactant.** If one of the reacting species is strongly adsorbed by the catalyst, it forms an almost complete layer, which is only removed when the particular constituent is nearly completely used up. Suppose the gas  $A$  is the one preferentially adsorbed; let  $\theta$  be the fraction of the surface covered by it, and suppose each molecule occupies  $n_1$  elementary spaces of the catalyst. The rate of condensation is equal to  $a_1(1 - \theta)^{n_1}\mu_1$ , where  $(1 - \theta)^{n_1}$  gives the probability of  $n_1$  adjacent spaces being vacant, since a molecule can only condense if this number of spaces is available. The rate of evaporation  $\nu_1$  may be regarded as almost constant when the surface is nearly completely covered, and so at equilibrium

$$a_1(1 - \theta)^{n_1} \mu_1 = \nu_1. \quad . \quad . \quad . \quad . \quad . \quad (\text{xxviii.})$$

If reaction occurs whenever a molecule of  $B$  condenses on the *free* surface, since sufficient  $A$  is always available to combine with it, then the rate of reaction is proportional to the rate of condensation; hence

$$\frac{dx}{dt} = ka_2(1 - \theta)^{n_1}\mu_2 \quad . \quad . \quad . \quad . \quad (\text{xxix.})$$

if each molecule of  $B$  condenses on  $n_2$  adjacent free spaces. Substituting the value for  $(1 - \theta)$  from equation (xxviii.), it follows that

$$\frac{dx}{dt} = ka_2\mu_2 \left( \frac{\nu_1}{a_1\mu_1} \right)^{n_2/n_1} . . . . . (\text{xxx}).$$

[illegible]

where  $p_A$  and  $p_B$  are the pressures of  $A$  and  $B$  respectively. The rate of reaction is thus proportional to the reciprocal of the pressure of the strongly adsorbed gas, to the power  $n_2/n_1$ .

**Carbon Monoxide-Oxygen Reaction.** For the reaction of carbon monoxide and oxygen on quartz glass the observations of Boden-



stein and Ohlmer, as already indicated, imply that  $n_2/n_1$  in equation (xxxi.) is unity, for

$$\frac{dx}{dt} = K \frac{[\text{O}_2]}{[\text{CO}]} = K \frac{p_{\text{O}_2}}{p_{\text{CO}}},$$

and Langmuir (1922) found a similar relationship to hold for the combination on the surface of platinum up to  $430^\circ \text{C.}$ , and pressures below 0.1 mm. of mercury. In these cases it is clear that the carbon monoxide is strongly adsorbed, and according to Hinshelwood the reaction presumably occurs when an oxygen molecule is adsorbed on a space adjacent to a carbon monoxide molecule. Langmuir was of the opinion, however, that combination resulted from the impact of a carbon monoxide molecule from the gas phase with one of the few adsorbed oxygen molecules (or atoms), but not when an oxygen molecule struck the adsorbed carbon monoxide. Provided the actual combination occurred very rapidly, this mechanism would lead to the reaction velocity being proportional to the rate at which oxygen molecules were condensed on the available surface, and the same velocity equation could be deduced as for the first mechanism proposed. It does not seem possible to decide between the two theories, but the former has at least the merit of greater simplicity. The fact remains, however, that the preferential adsorption of carbon monoxide has a poisoning effect; the greater the pressure of the carbon monoxide, within limits, the smaller the reaction velocity. Nitrous oxide behaves similarly to oxygen in many reactions: it is, therefore, of interest to mention that the rate of reaction between the former and carbon monoxide is proportional to  $[\text{N}_2\text{O}]/[\text{CO}]$  in quartz vessels at  $550^\circ$  (Bawn, 1935).

At temperatures above  $500^\circ \text{C.}$ , the carbon monoxide is not so strongly adsorbed on platinum as at lower temperatures; in fact the tendency for it to be adsorbed is almost the same as that of oxygen under the same conditions. If carbon monoxide is present in large excess, it will almost cover the surface, and the velocity of reaction will depend on the rate at which oxygen molecules condense; the rate of the reaction will thus be approximately proportional to the partial pressure of oxygen in the gas mixture. On



the other hand, if the oxygen is in excess it will be preferentially adsorbed, and the reaction velocity will vary roughly in direct proportion to the pressure of carbon monoxide.

On a silver surface, between  $80^{\circ}$  and  $140^{\circ}$ , the conditions are quite different: the reaction rate is proportional to the pressure of carbon monoxide, but independent of that of oxygen or of carbon dioxide (Benton and Bell, 1934). The results indicate a slow irreversible adsorption of oxygen, so that the surface is always nearly half covered with this reactant, but the adsorption of carbon monoxide is very small.

**The Hydrogen-Oxygen Reaction.** In a study of the reaction between hydrogen and oxygen on a platinum surface at temperatures up to about  $1600^{\circ}$  C., Langmuir found the results to be very similar to those obtained in the carbon monoxide and oxygen reaction. At low temperatures ( $0^{\circ}$  to  $300^{\circ}$  C.) the measurements were rather erratic, but the general conclusion was that the reaction rate was roughly proportional to the pressure of oxygen and inversely proportional to that of hydrogen; the latter substance is, therefore, preferentially adsorbed, and its action is similar to that of carbon monoxide. At high temperatures ( $400^{\circ}$  to  $1600^{\circ}$  C.) the kinetics of the reaction is again similar to that observed with carbon monoxide; both hydrogen and oxygen can be adsorbed to similar extents and the reaction velocity varies directly with the pressure of whichever of the two gases is present in smaller concentration. It may be concluded, therefore, that the reaction mechanism is the same as for the similar carbon monoxide-oxygen combination; either hydrogen and oxygen molecules adsorbed side by side react with one another (Hinshelwood), or combination occurs when hydrogen molecules from the gas phase strike adsorbed oxygen molecules, or atoms (Langmuir). In view of recent work, however (Hinshelwood and Donnelly, 1929; Tanner and G. B. Taylor, 1931), it appears that the hydrogen-oxygen reaction on platinum is much more complex than the results quoted here would imply.

The hydrogen-oxygen reaction on silver has been investigated by Bone and Wheeler at  $400^{\circ}$  C. (1906) and by Benton and Elgin at  $110^{\circ}$  C. (1926); both sets of investigators found that the rate



of combination is proportional to the hydrogen pressure and independent of that of oxygen. The catalyst was found to adsorb oxygen very strongly at  $110^{\circ}\text{C.}$ , whereas hydrogen was not taken up to any measurable extent ; hence it may be assumed, in order to account for the observed reaction rate, that the surface is completely covered with a layer of atomic oxygen, and that combination occurs as a result of a collision between a hydrogen molecule from the gas phase and an adsorbed oxygen atom. The rate of reaction will only depend on the rate at which hydrogen molecules strike the surface, and this is proportional to the partial pressure of the hydrogen gas. Benton and Elgin have calculated that only one impact in about  $10^{10}$  is effective in producing chemical reaction, and this they attribute to the fact that only a small proportion of the adsorbed oxygen atoms, namely those adjoining bare spaces, are in an active condition. An alternative explanation might be that oxygen is strongly adsorbed on certain " active " parts of the catalyst (p. 416), but hydrogen may become much less firmly adsorbed on other portions of the surface ; when a hydrogen molecule is attached to a space adjacent to one occupied by an oxygen atom, combination may be supposed to occur. Since the area covered by the oxygen will be independent of the pressure, but that occupied by the weakly adsorbed hydrogen is proportional to its pressure, the reaction rate will also be proportional to the latter.

In the reaction between hydrogen and oxygen on a gold surface at  $130^{\circ}$  to  $150^{\circ}\text{C.}$ , Benton and Elgin (1927) found the rate to be proportional to the pressure of oxygen and to the square of the hydrogen pressure ; that is

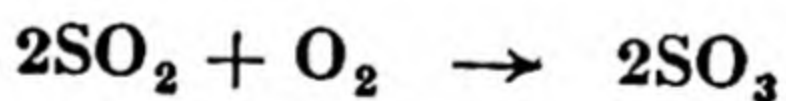
$$\frac{dx}{dt} = K[\text{H}_2]^2 [\text{O}_2].$$

This at first sight suggests an agreement with the simple type of mechanism for the reaction under discussion. During the course of the experiments it was found, however, that oxygen was strongly adsorbed by the gold, but hydrogen was not taken up to any appreciable extent ; under these conditions it will be shown subsequently that the reaction velocity expression should involve the *reciprocal* of the oxygen pressure, if the combination occurred



between hydrogen and oxygen adsorbed on adjacent spaces (equation xxx.). The dependence of the rate on the square of the hydrogen pressure may be attributed to the fact that reaction can only occur as a result of the simultaneous impact of two hydrogen molecules with one oxygen molecule. Since gold adsorbs oxygen in a very similar manner to silver, and neither adsorbs hydrogen, the reaction rate should be independent of the oxygen pressure, but with a gold catalyst it is actually proportional to this pressure. The discrepancy is difficult to understand, and Benton and Elgin suggested that it may be connected with a pressure variation of the speed at which oxygen is adsorbed on certain active parts of the surface. It is interesting to note that with both gold and silver catalysts the reaction velocity is also inversely proportional to the pressure of water vapour; the latter is obviously strongly adsorbed, and by occupying part of the surface there is less available for the oxygen. The reaction velocity is thus decreased in proportion to the surface occupied by the water vapour.

**Preferential Adsorption of Reaction Products.** An important example of the retardation of the reaction between two gases due to the adsorption of the product, rather than one of the reactants, is the well-known case



investigated by Bodenstein and Fink, and to which reference has been made earlier in the chapter (p. 396). It has been shown that the "diffusion" theory of these authors is probably not correct, but by making the assumption that the sulphur trioxide formed in the process is preferentially adsorbed by the catalyst it is possible to explain the observed reaction kinetics. If the area of the catalyst surface left free from sulphur trioxide is inversely proportional to the square root of the concentration of this gas, then the rate of reaction must also be inversely proportional to this quantity. In the presence of excess of sulphur dioxide, say, most of the surface left free from trioxide will be covered with dioxide, and hence the reaction velocity will also be directly proportional to the oxygen concentration (or pressure); that is



$$\frac{dx}{dt} = K \frac{[O_2]}{[SO_3]^{\frac{1}{2}}}$$

If oxygen is present in excess, the free surface will be covered with this gas, and the rate of combination will depend directly on the sulphur dioxide concentration. The high temperature coefficient of the reaction is due to the high heat of adsorption of sulphur trioxide, so that the amount adsorbed decreases rapidly with increasing temperature, leaving larger areas available for the adsorption of the dioxide or oxygen. This simple explanation of the sulphur dioxide-oxygen reaction is in harmony with the general theory developed by Langmuir and discussed in this chapter, and suffices to explain the observations of Bodenstein. The latter author has recently (1929) suggested a somewhat modified form of his "diffusion" theory. It is supposed, as in the Langmuir theory, that sulphur trioxide is adsorbed in a unimolecular layer on the catalyst, but the reacting molecules are assumed to have lateral mobility in this layer (p. 385). There is good reason to believe, as will be shown later, that catalytic reactions only occur at certain "active" spots on the surface, and according to Bodenstein it is the rate at which the oxygen, or sulphur dioxide, molecules can migrate over the surface to these active spots that determines the velocity of the reaction. If this rate is assumed to be inversely proportional to the square root of the sulphur trioxide pressure, a not improbable assumption, the kinetics of the reaction and the retarding effect of the trioxide may be explained.

### ACTIVE PARTS OF CATALYTIC SURFACES

The suggestion that different portions of a catalyst surface may have different properties has already been implied, and there is much evidence in favour of this view. In the first place, it must be realised that no surface is ideally smooth, and consequently the "residual field" will not be uniform; it will probably be greatest at the edges of crystals and at the summits of excrescences, or peaks, on the surface. An atom situated on a flat surface will be attached to similar atoms over a solid angle of  $180^\circ$ , but an



isolated atom at the apex of a peak will have a much smaller fraction of its electrostatic field shared with others ; the residual electrical field of the isolated atom will thus be much larger than the general value for other atoms constituting the surface. It is very probable, therefore, that the adsorptive power will be greatest on the peaks, and will not be uniform over the whole of the surface.

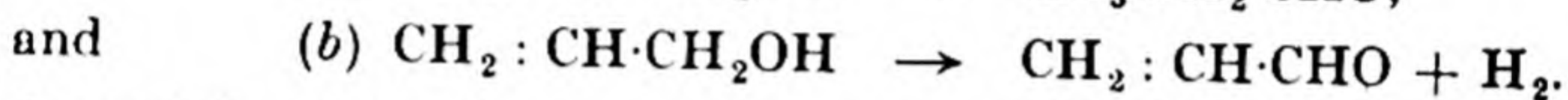
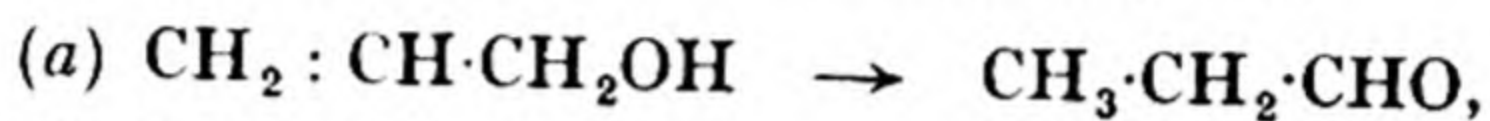
The absence of uniformity of a charcoal surface, for example, is shown by the discovery that there are three types of oxygen adsorption on this solid ; a small portion of the oxygen can be removed by evacuation, a larger portion is driven off as carbon dioxide at reduced pressures and comparatively low temperatures, and a third portion is only removed at high temperatures in the form of carbon monoxide and dioxide. Oxygen can also be adsorbed on nickel and copper surfaces in two ways, at least, under the same conditions ; in one type of adsorption the oxygen is apparently held rather loosely so that it is easily removed by hydrogen at low temperatures, whereas the remainder of the oxygen can only be removed by reduction at high temperatures.

The saturation capacity of a given adsorbent for different gases is not a constant, as one might expect if in each case a uniform unimolecular film were formed over the whole of the surface. For example, copper adsorbs more ethylene than it does hydrogen when saturation is attained, but nickel, on the other hand, adsorbs more hydrogen. For each of these metals either different parts of the surface are involved in the adsorption of the two gases, or else the adsorption capacities of the same portions vary with the nature of the gas. Pease (1923) found that traces of mercury diminish the adsorptive power of copper for various gases, but the extent of the decrease varies with the nature of the gas ; the adsorption of ethylene is reduced to 86 per cent., and that of hydrogen to about 20 per cent. of the value for the clean copper surface at a gas pressure of one atmosphere. The same quantity of mercury reduced the catalytic efficiency of the surface to less than one two-hundredth part of the original value. It is clear, therefore, that not only are there areas with different adsorptive capacities, but that not all the centres of adsorption are catalytically active. Confirmation of this conclusion is found in the observation that



traces of carbon monoxide, insufficient in amount either to cover the whole of the surface of the copper catalyst, or to displace all the adsorbed hydrogen or ethylene, can completely inhibit the reaction between the two last-mentioned gases (Pease and Stewart, 1925). In general, the amount of poison necessary to suppress the activity of a catalytic surface is much less than would be required to form a unimolecular film over the whole of it; only certain parts of the surface are thus effective in catalytic reactions.

If allyl alcohol vapour is passed over heated copper, it decomposes in two ways: one an isomerisation to propionic aldehyde, and the other a dehydrogenation to acrolein, viz.,



Constable (1926) has shown that if the copper catalysts are prepared by different methods, the relative extents to which the two alternative decompositions occur can be changed very markedly. Partially sintered copper is said to catalyse the isomeric change in preference to the dehydrogenation reaction. Similar observations have been made by Hoover and Rideal (1927) on the alternative decompositions of ethyl alcohol (see p. 395) on thoria catalysts; using a catalyst made by heating precipitated thorium hydroxide to  $120^\circ \text{C}.$ , the ratio of ethylene to acetaldehyde (and hydrogen) was 1.25 to 1, but with a supported catalyst obtained by saturating pumice with thorium nitrate and heating to  $400^\circ$  the ethylene reaction occurred almost exclusively. Reduction of pressure, with the unsupported catalyst, favours the ethylene reaction, but water vapour and acetaldehyde act as poisons for this reaction to a much greater extent than for the alternative decomposition. The conclusion to be drawn from the experiments of Constable and of Hoover and Rideal is that the catalysts have two different types of surface, each of which is responsible for the acceleration of a particular reaction.

The work of Hinshelwood and Prichard (1925) on the interaction of hydrogen and carbon dioxide on the surface of platinum at about  $1000^\circ \text{C}.$  provides striking evidence for the view that only parts of a surface are catalytically active. These



experiments incidentally bring to light the very important point that ordinary adsorption measurements do not necessarily indicate the particular adsorption which is effective in catalytic reactions. In the vicinity of  $1000^{\circ}$  the total adsorption of hydrogen by platinum is considerable, but that of carbon dioxide is negligible in comparison, yet it is the preferential adsorption of the latter which eventually decides the kinetics of the reaction ! It can only be concluded, therefore, that the reaction occurs at certain active parts of the catalyst, which adsorb carbon dioxide in preference to hydrogen, but these active portions can constitute only a small fraction of the total surface. The conclusion that carbon dioxide is strongly adsorbed is based on experiments made on the rate of the reaction



in the presence of concentrated sulphuric acid ; the object of the latter was to remove the water as fast as it was formed, and so render the reaction irreversible. It was found that when the pressure of carbon dioxide was low the reaction appeared to be normal, the velocity being proportional to the pressure of hydrogen and of carbon dioxide ; evidently under these conditions both gases are adsorbed more or less equally, and combination occurs between molecules adsorbed on adjacent spaces. As the carbon dioxide pressure is increased, however, the reaction velocity for any given pressure of hydrogen passes through a maximum value and then decreases ; at high carbon dioxide pressures the rate of reaction is described approximately by the equation

$$\frac{dx}{dt} = K \frac{[\text{H}_2]}{[\text{CO}_2]}.$$

This behaviour can only be explained by supposing that as the pressure is increased the carbon dioxide gradually displaces the adsorbed hydrogen, so that the former eventually covers nearly the whole of the active surface (compare the carbon monoxide-oxygen reaction, p. 412).

It is of further interest to mention that a platinum surface poisoned in this manner by carbon dioxide for the reaction between it and hydrogen remains quite unaltered in its catalytic action on



the decomposition of nitrous oxide ; it is clear, therefore, that this latter reaction occurs on portions of the platinum not involved in the former process. The same conclusion is reached from Hinshelwood's discovery that a platinum wire poisoned by hydrogen for the decomposition of ammonia remains unaffected for the catalytic thermal dissociation of hydrogen iodide ; the latter is unable to displace hydrogen gas from the surface, and so apparently its decomposition occurs at points not involved in the ammonia dissociation. Experiments with a copper catalyst have shown that the portions which are most active for the hydrogenation of ethylene are not those upon which the decomposition of nitrous oxide occurs (Russell and Ghering, 1935).

**Uniformity of Surfaces.** Although the evidence so far suggests that many catalytic surfaces have portions of different activities, there are some interesting results indicating that in some instances such surfaces are uniform. The constancy of the heat of adsorption of hydrogen on copper (p. 386) may be explained by the mobility of the adsorbed molecules on the surface, but it is doubtful if the results described below can be interpreted in the same manner. Methyl alcohol is dehydrogenated on a zinc surface, but Steacie and Elkin (1938) have made the surprising observation that the rate of reaction shows no abrupt change when the zinc is melted ; that is to say, the surface of liquid zinc is just as effective a catalyst as that of the solid. It is apparent, therefore, that the catalysis cannot be limited to any specific part of the surface. Some years ago Vavon and Husson (1922) stated that a colloidal platinum catalyst could be poisoned in stages by carbon disulphide, so that it progressively lost the power of reducing first acetophenone, then nitrobenzene and finally benzene. This statement has been widely quoted as evidence for the heterogeneity of catalytic surfaces, but a re-investigation of the subject by Maxted *et al* (1933-35) has cast doubt on its accuracy. It appears that the catalytic effect of platinum black is definitely diminished as a consequence of poisoning by mercuric salts or by carbon disulphide, but the extent of the reduction is the *same* for a number of hydrogenation processes, *e.g.*, of nitrobenzene, acetophenone, benzene, and crotonic, oleic and benzoic



acids, in spite of the fact that the rates of reaction are different in the various cases. Such a result clearly indicates that the parts of the surface involved in catalysis have a uniform activity. Further, the heat of activation for the decomposition of hydrogen peroxide and for the hydrogenation of liquid crotonic acid on finely divided platinum is the same before and after the catalytic activity has been reduced by heat treatment. Similarly, although the effectiveness of platinum for the decomposition of hydrogen peroxide can be reduced to one-tenth of its initial value as a result of poisoning by mercuric chloride, the activation energy remains almost constant. If some parts of the catalyst were more active than others a difference in the energy required to bring about reaction might have been expected (*vide infra*). Although these observations imply that there is in these instances an absence of heterogeneity in the active parts of a catalyst, it does not follow that the *whole* of the surface is always effective: there is little doubt that there are generally so-called "active centres" on the catalytic surface and it is necessary to consider the nature and function of these centres.

### NATURE OF ACTIVE CENTRES

Taylor (1925) first made the suggestion that the isolated atoms with high residual fields, to which reference has already been made (p. 416), would be the "active" points on a catalytic surface. Although these atoms may be the most effective adsorbents, it does not follow that they are always those at which chemical reaction is favoured. Many of the experiments already described show that the powerful adsorption of a gas, presumably on the "unsaturated" atoms, does not necessarily inhibit the catalytic influence of the surface for a reaction not involving that gas.

The decrease of catalytic activity of a surface resulting from heating has been ascribed to the reduction in the number of isolated atoms as a result of sintering; the adsorptive power of the surface is reduced at the same time. It must be remembered, however, that heating will cause a general reduction in the surface



area, so that the catalytically active portions, whether peaks or otherwise, will probably be reduced in extent. While admitting with some certainty that many, if not all, catalytic surfaces are non-uniform, it must be concluded that sufficient evidence is not yet available to allow the active parts to be definitely identified with peaks or excrescences on the surface.

A modification of this view-point is, however, gaining ground amongst workers in the field of catalysis; it is supposed that the active centres are to be identified with lines of demarcation, for example, the edges of crystals and grain boundaries (Schwab and Pietsch, 1929), or with cracks or imperfections in the crystals of catalyst (Smekal, 1929). All these positions will be "unsaturated" in the same sense as the isolated atoms postulated by Taylor, but not perhaps to the same extent. An interesting experiment by Felman and Adikhari (1925) provides evidence that chemical reaction tends to occur at phase boundary or demarcation lines; a molecular beam of iodine (cf. p. 141) was allowed to impinge on a drop of mercury, which thus became covered with an adsorbed layer of molecules. When the side of the drop opposite to the beam was touched with a crystal of mercuric iodide, thus producing a phase boundary line, the crystal commenced to grow at this line, but at no other point was mercuric iodide formed. It appears that the iodine molecules migrate over the mercury surface but only react at a line of demarcation. Schwab and Pietsch further support their "adlineation" hypothesis by means of photographs of catalytic surfaces which suggest that the active "centres" are really lines between adjoining crystals.

### FUNCTION OF ACTIVE CENTRES

The next point to consider in the analysis of the problems of heterogeneous catalysis is why the molecules attached to certain parts of a surface are in a particularly reactive state; partial answers to this question have been suggested from various lines of research, some of which will now be considered. It appears that the molecules of reactant are always activated in some manner by the catalyst, but the nature of this activation probably varies in



reactions of different types. The various possibilities to be discussed are, therefore, not to be regarded as mutually exclusive, but as different aspects of what is probably the same fundamental phenomenon.

In the first place, it appears that adsorbed molecules may be oriented upon or attached to the surface atoms in a particular manner, so that the reactants become more easily decomposed or attacked. Norrish (1923) found that the well-known combination of ethylene and bromine vapour, or chlorine, was really a heterogeneous reaction; it occurred readily on a glass surface, and on one of cetyl alcohol, and still more rapidly on stearic acid, but hardly at all on paraffin wax. It seems, therefore, that a polar surface facilitates this reaction; presumably the ethylene is adsorbed on the polar groups of the surface molecules, and there results an electronic drift, or polarisation, in the ethylene which renders it reactive. Although Williams (1932) concludes that the reaction is a complex one and probably involves a chain mechanism initiated at the surface, it is still possible that distortion of the electronic arrangement in the reactants may be regarded as one of the possible modes of activation brought about by a catalyst.

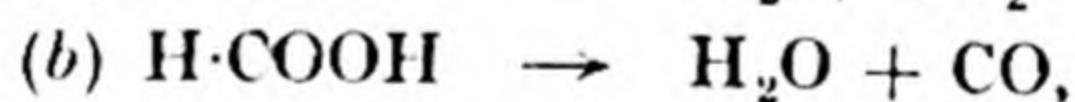
**Molecular Distortion.** Palmer and Constable (1920-28) have studied the dehydrogenation of alcohols to the corresponding aldehydes on copper surfaces; they noted that the rate of decomposition of the primary ethyl, propyl, butyl, *isobutyl* and *isoamyl* alcohols on a given catalyst at a definite temperature was constant and independent of the length of the hydrocarbon-chain. The temperature coefficient of the reaction was also the same for all the alcohols. The same reaction rate was found in the dehydrogenation of allyl alcohol which contains the  $-\text{CH}_2\text{OH}$  grouping, but *isopropyl* alcohol, a secondary alcohol with a  $-\text{CHOH}$  group, decomposed five times as fast. The conclusion is drawn from these results that the copper catalyst exerts its activating action on the  $-\text{CH}_2\text{OH}$  grouping of a primary alcohol. It is supposed that the arrangement of the active centres of the copper is such that the distance apart of the hydrogen and oxygen atoms in the  $-\text{OH}$  group is strained beyond the normal value; the hydrogen atom is activated in this way and so readily breaks off from the rest of the



molecule. Another hydrogen atom, originally attached to the carbon atom of the  $-\text{CH}_2\text{OH}$  group, can now readily leave the unstable residue, so molecular hydrogen can form, and generally an aldehyde molecule remains. The activation by the surface, which renders the molecule reactive, is in this case definitely connected with orientation on the surface and the resulting strain in the  $\text{O}-\text{H}$  linkage; there seems no other method of accounting for the independence of the reaction velocity of the length of the hydrocarbon chain attached to the  $-\text{CH}_2\text{OH}$  group. The variable activity of copper surfaces prepared in different ways is attributed to the alteration in the spacing of the active centres, so that the amount of distortion, and hence activation, varies. Since alcohols can undergo an alternative decomposition, *e.g.*, ethyl alcohol into ethylene and water on thoria, it must be supposed that on certain catalysts a different type of orientation is possible. This alternative orientation apparently produces a strain in the  $\text{C}-\text{O}$  linkage so that another mode of decomposition results. Adkins and Nissen (1923) have found that alumina prepared in different ways has varying catalytic activity in the decomposition of formic acid; this variation is not only in the total rate of the reaction, but the relative rates of the two alternative processes

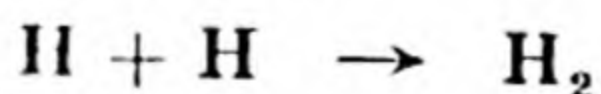


and

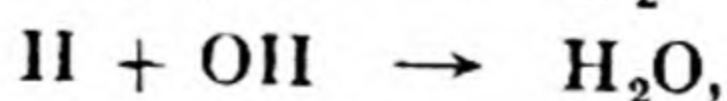


are markedly affected. It appears, therefore, that the alumina catalysts may not only differ in the spacing of the active centres, but that the type of orientation favoured may also vary.

Taylor (1931) states that the catalysts which favour the dehydrogenation reaction of alcohols, leading to the formation of aldehyde and hydrogen, are just those effective in bringing about the union of hydrogen atoms, whereas others favouring the dehydration process, leading to olefine and water, are most effective in the combination of hydrogen atoms and hydroxyl radicals (Taylor and Lavin, 1930). These results imply that in the two alternative decomposition processes of the alcohol the final stages are



and





respectively ; this is quite in harmony with the views expressed here concerning the alternative orientations and strains in the molecule brought about by different surfaces.

**Theory of Multiple Adsorption.** Observations on the alternative decompositions of a given compound on different catalysts or on different portions of the same catalyst, have led Burk (1926) and Balandin (1929) to propose a theory of multiple adsorption to account for the activation of a molecule by a catalyst ; it is supposed that if a molecule is adsorbed at one point only it is not activated, but if adsorbed at two or more points the molecule may become distorted, strained or, in the extreme, torn apart. The tendency to complete the decomposition of the adsorbed molecule will thus be considerably greater than for a normal molecule, and the reaction velocity will be much greater than for the uncatalysed reaction. Balandin attempts to explain the alternative modes of decomposition of alcohols by assuming that in the dehydrogenation process two hydrogen atoms are attached at one point and the rest of the molecule at another, whereas in the dehydration reaction the hydrogen and hydroxyl are adsorbed at one point and the remainder in an adjacent place. This is, however, not the only mechanism involving multiple adsorption which would be equally in harmony with the observations. Frölich (1928) has attempted to correlate the influence of various promoters and the dimensions of the unit crystal lattice of a metal catalyst ; a change in the size of the lattice would presumably affect the distance apart of active centres, and so influence the strain exerted on adsorbed molecules. The results obtained so far are not convincing, but the idea is certainly attractive, and would account for the action, in some cases at least, of promoters, and for the varying activity of catalysts prepared in different ways.

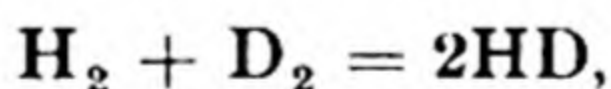
It is perhaps unnecessary to emphasise that the idea of activation by distortion implies a somewhat rigid attachment between the adsorbed molecules and the surface ; since the concept of lateral mobility is becoming generally accepted it appears that some modification may be necessary. There is a possibility, however, that the type of adsorption leading to appreciable strains



in a molecule, and which must be of a chemical nature, does not permit of appreciable freedom of movement.

**Adsorption of Atoms.** Taylor (1926) has suggested, in agreement with the views of Langmuir, that a catalytic surface is able to hold, at least temporarily, *atoms* as distinguished from molecules of the resultants of a reaction. It is known that hydrogen atoms frequently evaporate off from a metal filament heated in hydrogen gas, and Gauger (1924), Wolfenden (1926) and Kistiakowski (1926) have concluded from a study of the ionisation potentials of hydrogen and nitrogen adsorbed on various metals, that the gases were present on the surface in the atomic form.

The conversion of ortho- to para-hydrogen in the presence of a catalyst is also important from Taylor's point of view. In the absence of a catalyst this change takes place very slowly, but in the presence of charcoal (Bonhoeffer and Harteck, 1929) or of a special form of nickel (Taylor and Sherman, 1931) the inter-conversion takes place readily. Similarly the reverse change of the para- to the ortho-form can be brought about readily on the surfaces of certain oxides (Taylor and Sherman, 1932). The slow reaction without a catalyst is due to the difficulty of reversing the proton spins in the hydrogen molecule, but if the catalytic surface is able to bring about dissociation into atoms its efficiency is easily explained, since the resulting atoms are able to unite to furnish molecules with the appropriate proton spins. It is perhaps significant that surfaces showing so-called "activated" adsorption of hydrogen, which has been attributed to the presence of atoms (p. 391), are the best catalysts for the ortho-para conversion (see "Recent Advances in General Chemistry," Chapter III.). The heterogenous reaction between hydrogen and deuterium,

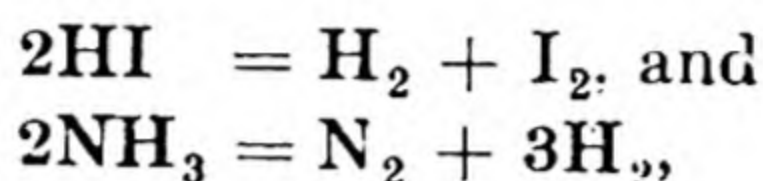


almost certainly takes place through the intermediate formation of atoms; chromium sesquioxide and nickel, both of which show activated adsorption, are effective catalysts even at low temperatures (Gould, Bleakney and Taylor, 1934). It is probable, too, that a number of catalytic exchange reactions between deuterium gas and compounds containing light hydrogen take place *via*

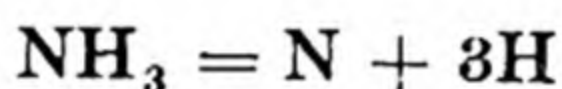


the intermediate formation of atoms, possibly in the form of surface hydrides (Barrer, 1935, 1936; Farkas, 1936).

**Heterogeneous Unimolecular Reactions.** Hinshelwood and his co-workers have observed that certain gas reactions, *e.g.*,



which are bimolecular if homogeneous, are undoubtedly unimolecular when they occur as heterogeneous processes on the surface of a catalyst. If these reactions were to be unimolecular when homogeneous, the energy of activation required would have to be very large on account of the large amount of heat absorbed in the dissociation of hydrogen, oxygen and nitrogen into atoms. For the unimolecular decomposition

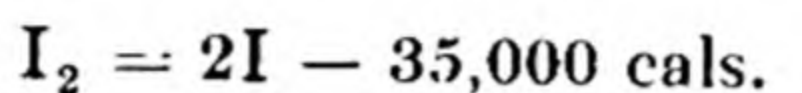
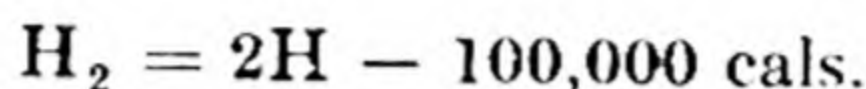
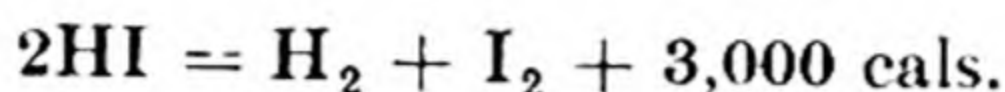


the heat absorbed is about 291,000 cal. per gm. mol., or 97,000 cal. per N — H linkage, and the heat of activation would need to be at the very least equal to this value; the probability of the reaction occurring would be extremely small. The heat absorbed in the corresponding bimolecular reaction is only 11,000 cal. per gm. mol., and so this type of decomposition will take place far more readily. The fact that the unimolecular decomposition does occur on the surface of a catalyst shows that the surface can adsorb atoms of nitrogen and hydrogen, and presumably the heat absorbed in the formation of an adsorbed atom is much less than for a free atom; in view of the fact that heat is evolved on adsorption this is to be expected. The heat of activation is then correspondingly lowered, so that the reaction can occur more readily.

The fact that substances may be held on the surface of a catalyst in atomic form has important consequences, as may be seen from Taylor's consideration of a possible mechanism for the decomposition of hydrogen iodide; this is not the only one possible, but it is taken as an example because the necessary data for the discussion are available. From observations on the initial heat of adsorption of hydrogen on platinum, and the known value



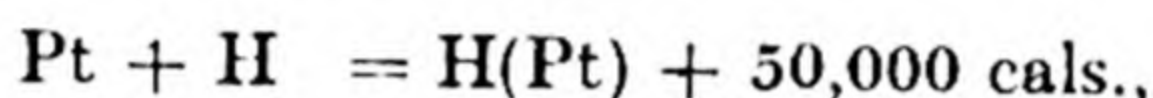
of the heat of dissociation of hydrogen into atoms, it is estimated that the heat of adsorption of atomic hydrogen on the active centres of platinum is about 53,000 cal. per gm. atom. From the known (approximate) heats of the following reactions



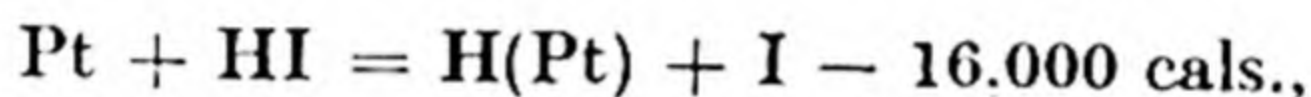
it follows that



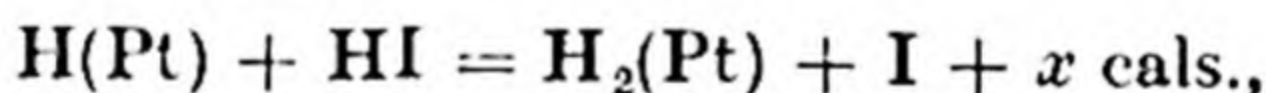
the heat of activation for this unimolecular reaction must therefore be very large. The heat of adsorption of hydrogen atoms is about 50,000 cal. ; this may be written



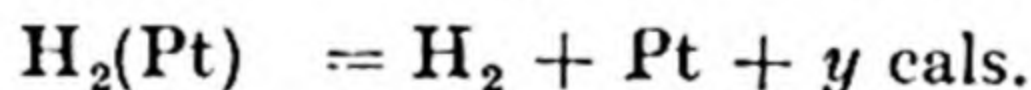
then



and the unimolecular decomposition with the formation of *adsorbed* atomic hydrogen comes within the realm of reasonable possibility. The adsorbed atoms must be desorbed from the surface, and Taylor suggests as a possible mechanism that the removal occurs as the result of an impact by a hydrogen iodide molecule, or possibly reaction with such a molecule adsorbed adjacent to a hydrogen atom. The following processes then occur



and



The quantity  $y$  cal. represents the heat of desorption, which is numerically equal to the heat of adsorption, of molecular hydrogen ; this is only known very approximately to be something between  $-10,000$  and  $-25,000$  cal., but it is the order of magnitude which is of importance. Using this value for  $y$ , and the known heats of the other reactions already given, it is seen that  $x$  is between  $-6,000$  and  $+9,000$  cal. With the adsorption mechanism suggested, therefore, a reaction requiring a heat absorption of 66,000 cal. in a single change is converted into one of three stages none of which requires more than about 25,000 cal. ;



none of these stages is highly endothermic and the chances of the reaction occurring are probably greatly increased. The ability of the catalyst to adsorb hydrogen atoms provides a mechanism, therefore, for the unimolecular decomposition of hydrogen iodide.

In the decomposition of ammonia the heat absorbed in the breaking of an N — H linkage if an adsorbed hydrogen atom is formed can be shown to be about 44,000 cal., instead of 97,000 cal. if free atoms result. There is no simple mechanism in this process for the removal of hydrogen atoms from the surface of the catalyst; no reaction with ammonia can occur, since the heat required would be of the order of 200,000 cal. The hydrogen atoms, therefore, remain on the surface until removed by evaporation or combination with adjacent atoms. This theory provides a thermochemical explanation of the observation made by Hinshelwood and Burk (see p. 405) that in the decomposition of ammonia on platinum the surface is poisoned by hydrogen, probably in the form of atoms.

## THE ENERGY OF ACTIVATION

Although Taylor's theory accounts for the fact that a heterogeneous unimolecular reaction is much more probable than a homogeneous one, it still does not explain why the heterogeneous catalytic reaction occurs more readily than a homogeneous bimolecular reaction. Some light is thrown on this problem by the work of Hinshelwood. It is known (Chapter V.) that for a homogeneous reaction the molecules must acquire a definite minimum heat of activation before they can react or decompose, and it is not improbable that the same applies to catalytic heterogeneous reactions. The Arrhenius equation (p. 262) may be written

$$\frac{d \ln k}{dT} = \frac{E_a}{RT^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (\text{xxxii.})$$

where  $k$  is the velocity constant of the reaction, and  $E_a$  is the apparent heat of activation. Hinshelwood, following Polanyi (1921), has shown, however, that  $E_a$  is not equal to the true heat of activation  $E_t$ , and for a single reacting species with products which do not retard the reaction







equilibrium that the heat of adsorption or desorption ( $\lambda$ ) must be zero under these conditions. For an unretarded reaction, therefore,  $E_a$  and  $E_t$  must be equal if the active surface is saturated, and the reaction is apparently of zero order (p. 400). Taking these facts into consideration Hinshelwood has drawn up the following Table LXIII. comparing the heats of activation for a number of bimolecular homogeneous reactions with those required for the same reaction occurring as a unimolecular change on a catalyst. (The fact that the homogeneous decomposition of nitrous oxide is to a great extent unimolecular does not affect the main argument.)

TABLE LXIII.

*Heats of Activation of Homogeneous and Heterogeneous Reactions*

Reaction.	Total Activation. Homogeneous Bimolecular.	Total Activation. Heterogeneous Unimolecular.
Thermal decomposition of—		
Hydrogen iodide .	44,000 cal.	25,000 cal. (gold)
Nitrous oxide .	58,500 „	(29,000 „ (gold)
Ammonia . .	78,000 „	(32,500 „ (platinum)
		39,000 „ (tungsten)

In these decompositions the heat of activation for the heterogeneous reactions is approximately half the value for the homogeneous bimolecular processes, and so the probability of a molecule acquiring the necessary energy to allow it to react is very much greater in the heterogeneous reaction. It is thus seen that because the catalyst allows the unimolecular reaction to occur, the probability of its occurrence, and hence the reaction rate, is markedly increased.

**Homogeneous and Heterogeneous Reactions.** Apart from the question of the relative heats of activation of homogeneous bimolecular and heterogeneous unimolecular reactions, it is to be anticipated that the energy of activation of a heterogeneous process will in any case be lower than that of the corresponding homo-



geneous reaction. This subject has been discussed (London, 1929 ; Polanyi, 1929 ; Burk and Daus, 1931) along the lines followed in the theoretical interpretation of the energy of activation for homogeneous reactions (p. 276). If a strain is produced in a molecule of reactant as a result of being adsorbed on a catalytic surface its potential energy is thereby increased, so that the additional energy which must be supplied before the top of the "energy pass" can be reached is less than would have been the case for a molecule not on the surface. The energy of activation required for reaction should thus be less for a molecule adsorbed on a catalyst than for the corresponding homogeneous change. A preliminary attempt at calculating activation energies for heterogeneous processes, by the use of London's equations for the total energy of a system of several nuclei and the Morse equation for the potential energy of a molecule (p. 216), has been made by Sherman and Eyring (1932), but it is yet too soon to assess the value of the treatment adopted.

Confirmation for the view, that the increased reaction velocity is due to the decrease in the energy of activation, could be obtained if it were shown definitely that the rate was high with those catalysts on which the necessary heat of activation was low. Unfortunately differences in the state of the surfaces make the comparison almost impossible. Another test might be to consider the relative rates and respective heats of activation of two reactions occurring simultaneously on the same catalyst ; such a comparison would be of little value, however, as the two processes undoubtedly occur on quite different active areas.

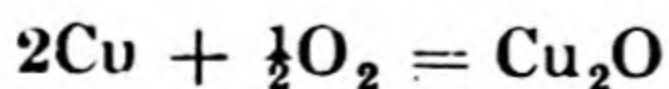
### OTHER CATALYTIC FACTORS

**Catalysis and Quantum Mechanics.** In the discussion of homogeneous reactions it has been mentioned (p. 279) that according to the requirements of quantum mechanics there is a definite probability that molecules having energy smaller than the amount necessary for activation will surmount the energy pass, and so react. For a homogeneous reaction this probability is negligibly small during the period of a collision between two

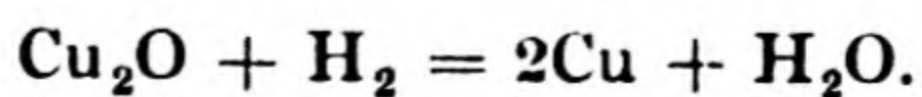


molecules, unless the energy is very close to the activation value. It has been suggested, however, that a catalyst, in addition to its other functions, may serve the purpose of keeping the reactants in contact long enough for the probability of their surmounting the energy pass to become appreciable (Born, 1931). That is to say, the catalyst assists the reacting molecules to "tunnel" through the energy hill in order to reach the valley represented by the products of the reaction. It is difficult to estimate to what extent, if at all, this factor is responsible for the acceleration of reactions by catalysts, but it is an interesting concept and is capable of mathematical development. Cremer and Polanyi (1932) consider that in hydrogenation catalysis this tunnel effect should be more marked with the lighter than with the heavier isotope of hydrogen; the latter should thus tend to concentrate in the residual gas. Experiments on the reduction of styrene failed, however, to reveal any excess of deuterium in the residue.

**Intermediate Compounds and Catalysis.** The theory that intermediate compounds play a role in catalysis is often suggested in connection with homogeneous reactions, but it has generally been regarded as of minor importance in heterogeneous gas reactions, although the formation of an adsorbed layer, involving the sharing of electrons, between the gas molecules and atoms of catalyst, differs only from the formation of a definite intermediate compound by the fact that a separate phase is not formed. Some interesting observations by Wilkins and Bastow (1931) show, however, that in the hydrogen-oxygen reaction on copper at 200° there is very strong evidence that cuprous oxide is formed as an intermediate compound, and is consequently the factor responsible for the catalytic reaction. The rates of oxidation of copper to cuprous oxide by oxygen and of the reduction of cuprous oxide to copper by hydrogen have both been determined by independent experiments, and from the results it is possible to calculate the rate of formation of water if a mixture of hydrogen and oxygen is passed over heated copper, provided the reaction mechanism is



followed by





At  $250^{\circ}$  the observed rate of reaction was almost identical with that calculated, although the rapid sintering of the copper at this temperature made the results unreliable. At low temperatures the observed rates were always somewhat greater than the calculated values, the differences increasing with decreasing temperature, but the closeness of the results was sufficient to warrant the conclusion that a large proportion of the catalytic reaction was occurring through the formation of cuprous oxide as an intermediate compound. It is not impossible that a similar mechanism may be operative in other catalytic processes.

**Supply of Energy by Catalyst.** There is another factor requiring consideration which may be operative in increasing the speed of catalytic processes. If the reacting molecules do not decompose immediately, they may remain on the surface for a short interval of time; in the course of this stay some of them may possibly absorb energy from the atoms of the catalyst in amounts sufficient to activate them. The number of molecules possessing amounts of energy greater than the heat of activation will be in excess of that which would result from the normal distribution according to Maxwell's law (p. 264). This factor will cause an increase in the reaction rate for the heterogeneous process above that for the homogeneous reaction, apart from any simultaneous reduction in the heat of activation. For the heterogeneous decomposition of methane, on the surface of a heated platinum wire coated with alkaline earth oxide investigated by Schwab and Pietsch (1926), it was found that the reaction velocity was much greater than could be accounted for by the number of molecules possessing the appropriate amount of energy striking the wire. It was concluded, therefore, that many of these molecules remained on the heated wire for an appreciable time, and derived sufficient energy from it to permit them to decompose.

In the bimolecular decomposition of acetaldehyde on heated wires (p. 407), Hinshelwood and Allen found that the heat of activation was independent of the nature of the catalyst, and incidentally was almost the same as for the homogeneous bimolecular reaction. Similar results were obtained by H. A. Taylor and Schwartz (1931) for the decomposition of diethyl ether on platinum



and tungsten filaments at  $700^{\circ}$ — $900^{\circ}$ . In these cases it seems that the reactant molecules are held rather loosely by the metal surface so that its heat of activation is not affected; the catalyst atoms then serve the purpose only of supplying energy to the adsorbed molecules in amounts sufficient to activate them. Mention has already been made that from a study of the kinetics of the acetaldehyde reaction (p. 407) it appears that decomposition occurs when a molecule adsorbed on the surface is struck by one from the gas phase.

A surface may act catalytically by removing, as well as by supplying energy: it has been mentioned in Chapter V. that certain reactions can only occur as three-body collisions, because the heat of the reaction concerned would otherwise cause the product to dissociate into its constituents (p. 284); a solid surface, *e.g.*, the wall of the reaction vessel or any other surface introduced into the reacting system, may also serve to deprive the product of its excess energy and so prevent decomposition. In a sense, therefore, the surface acts as a catalyst, although, strictly speaking, the chemical reaction is a homogeneous one. The same statement might be made with reference to chain reactions which are initiated at the surface but continue in the gas phase (p. 312).

## CONCLUSION

In the latter part of this chapter a number of factors has been examined, all or some of which may have an influence in catalytic reactions involving gases; in addition, of course, other influences may be at work. Various authors have suggested the possibility that ionisation is an important factor in the mechanism of catalysis. It is true that good catalysts often show a strong positive ion or electron emission, and that often catalytic reactions are accompanied by measurable electron currents, but there is not yet sufficient evidence to connect definitely the mechanism of a heterogeneous reaction with an ionisation process. In view of the very widespread occurrence of catalytic actions compared with the rarity of homogeneous processes Hinshelwood has suggested the possibility that there is some general influence of catalysts,



presumably not yet elucidated, superimposed upon all the specific influences which operate for particular cases. The whole problem is indeed a complex one, but decided progress has been made in recent years towards its clarification. Although certain advances have also been recorded in the study of promoters, the conclusions reached are more speculative than definite, and so the subject will not be pursued further here.

## REFERENCES

- ABORN and DAVIDSON. *J. Physical Chem.*, 1930, **34**, 422.  
 ADKINS *et al.* *J. Amer. Chem. Soc.*, 1923, **45**, 809 ; 1926, **48**, 1671 ; 1929, **51**, 2440.  
 BACHMANN and TAYLOR. *J. Physical Chem.*, 1929, **33**, 447.  
 BALANDIN. *Z. physikal. Chem.*, 1929, **B2**, 289 ; **B3**, 167.  
 BENTON and ELGIN. *J. Amer. Chem. Soc.* 1926, **48**, 3027 ; 1927, **49**, 2426.  
 BENTON and WILLIAMS. *J. Physical Chem.*, 1926, **30**, 1487.  
 BODENSTEIN. *Z. physikal. Chem.*, 1929, **B2**, 345.  
 BORN and WEISSKOPF. *Ibid.*, 1931, **B12**, 206.  
 BURK *et al.* *J. Physical Chem.*, 1926, **30**, 1134 ; 1928, **32**, 1601 ; 1931, **35**, 1461 ; *Proc. Nat. Acad. Sci.*, 1927, **13**, 67.  
 CONSTABLE. *Proc. Roy. Soc.*, 1925, **107A**, 270, 279 ; 1925, **108A**, 855 ; 1926, **110A**, 283 ; 1926 **113A**, 254 ; *J. Chem. Soc.*, 1927, 1578, 2995.  
 CREMER and POLANYI. *Z. physikal. Chem.*, 1932, **B19**, 443.  
 DIXON. *J. Amer. Chem. Soc.*, 1931, **53**, 1763, 2071.  
 DOHSE. *Z. Elektrochem.*, 1930, **36**, 677.  
 DOHSE and KÄLBERER. *Z. physikal. Chem.*, 1929, **B5**, 131.  
 DONNELLY. *J. Chem. Soc.*, 1929, 2438.  
 FELMAN and ADIKHARI. *Z. physikal. Chem.*, 1925, **131**, 347.  
 FRAZER. *J. Physical Chem.*, 1930, **34**, 2120\*.  
 FRENKEL. *Z. Physik*, 1924, **26**, 117.  
 FRÖLICH. *J. Ind. Eng. Chem.*, 1928, **20**, 694, 1327 ; 1929, **21**, 109.  
 GARNER and VEAL. *J. Chem. Soc.*, 1935, 1487.  
 HAILES. *Trans. Faraday Soc.*, 1931, **27**, 601.  
 HINSHELWOOD *et al.* *Proc. Roy. Soc.*, 1924, **106A**, 292 ; 1925, **108A**, 211 ; 1928, **121A**, 141 ; *J. Chem. Soc.*, 1923, **125**, 1014, 2725 ; 1924, **125**, 303 ; 1925, **127**, 327, 806, 1105, 1552, 2896 ; 1926, 1707 ; 1929, 1727 ; *Ann. Reports*, 1927, **24**, 335\* ; 1930, **27**, 34\* ; 1931, **28**, 23\* ; "Kinetics of Chemical Change in Gaseous Systems," 1934\*.  
 HOGNESS and JOHNSON. *J. Amer. Chem. Soc.*, 1932, **54**, 3583.  
 KUNSMAN. *Ibid.*, 1928, **50**, 2100.  
 LANGMUIR. *Ibid.*, 1918, **40**, 1361 ; *Trans. Faraday Soc.*, 1922, **17**, 621.  
 LONDON. *Z. Elektrochem.*, 1929, **35**, 552 ; *Z. physikal. Chem.*, 1930, **B11**, 222.  
 MAXTED. *J. Chem. Soc.*, 1933, 502 ; 1934, **26**, 672 ; 1935, 393, 1190 ; *Ann. Reports*, 1935, **32**, 109\*.  
 MITCHELL. *J. Chem. Ed.*, 1932, **9**, 261\*.  
 NORRISH. *J. Chem. Soc.*, 1923, **125**, 3006.  
 PALMER. *Proc. Roy. Soc.*, 1929, **122A**, 487.  
 PEARCE. *J. Physical Chem.*, 1932, **36**, 1969.



- PFASE. *J. Amer. Chem. Soc.*, 1923, 45, 1196, 2235, 2296.  
PEASE and STEWART. *Ibid.*, 1925, 47, 1235 ; 1927, 49, 2783.  
POLANYI. *Z. Elektrochem.*, 1921, 27, 143 ; 1929, 35, 561 ; *J. Soc. Chem. Ind.*, 1935, 54, 123T.  
REID. *J. Physical. Chem.*, 1927, 31, 1120\*.  
RIDEAL *et al.* *J. Chem. Soc.*, 1922, 121, 309 ; 1935, 1701.  
SAUTER. *Z. Elektrochem.*, 1930, 36, 874 ; "Heterogene Katalyse," 1930\*.  
SCHWAB. *Z. physikal. Chem.*, 1927, 128, 161 ; "Katalyse vom Standpunkt der chemischen Kinetik," 1931\*.  
SCHWAB and PIETSCH. *Ibid.*, 1926, 121, 189 ; 1929, B1, 385 ; 1929, B2, 262, 1931, B13, 13 ; *Z. Elektrochem.*, 1929, 35, 573\*.  
SHERMAN and EYRING. *J. Amer. Chem. Soc.*, 1932, 54, 2661.  
SMEKAL. *Z. Elektrochem.*, 1929, 35, 567 ; *Z. physikal. Chem.*, 1929, B5, 60.  
STEACIE and ELKIN. *Proc. Roy. Soc.*, 1933, 142A, 457.  
STRANSKI. *Z. Elektrochem.*, 1930, 36, 25.  
ZUR STRASSEN. *Z. physikal. Chem.*, 1934, 169, 81.  
TANNER. *J. Amer. Chem. Soc.*, 1932, 54, 2171.  
TANNER and TAYLOR, G. B. *Ibid.*, 1931, 53, 1269.  
TAYLOR, H. A., and SCHWARTZ. *J. Physical Chem.*, 1931, 35, 1044.  
TAYLOR, H. S., *et al.* *Proc. Roy. Soc.*, 1925, 108A, 105 ; 1926, 113A, 77 ; 1927, 117A, 131 ; *J. Physical Chem.*, 1924, 28, 897 ; 1926, 30, 145\* ; *Z. Elektrochem.*, 1929, 35, 542\* ; *J. Amer. Chem. Soc.*, 1921, 43, 1273 ; 1931, 53, 578, 1614, 3604 ; 1932, 54, 602 ; 1934, 56, 586, 2254, 2259 ; *Trans. Faraday Soc.*, 1932, 28, 247.  
VOLMER. *Z. Elektrochem.*, 1929, 35, 555.  
WILKINS. *J. Chem. Soc.*, 1931, 330.  
WILKINS and BASTOW. *Ibid.*, 1931, 1525.  
WILKINS and RIDEAL. *Proc. Roy. Soc.*, 1930, 128A, 394.  
WILLIAMS. *J. Chem. Soc.*, 1932, 1747, 1758.

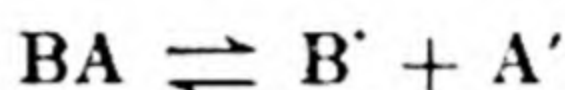
\* Review papers and books, wherein further references are to be found, are marked by an asterisk.



## CHAPTER IX

### STRONG ELECTROLYTES

IN a solution of an electrolyte BA it may be assumed that there is an equilibrium between the ions, B' and A', and the molecules of undissociated BA, thus



and if the law of mass action is applicable it should follow that

$$\frac{[B'] [A']}{[BA]} = \text{a constant } (k); \quad . \quad . \quad . \quad . \quad . \quad (i.)$$

this is called the ionisation, or dissociation, constant of the electrolyte. If  $c$  is the concentration in gm. mols. per litre and  $\alpha$  the degree of dissociation of the solute, then

$$[B'] = \alpha c, [A'] = \alpha c \text{ and } [BA] = (1 - \alpha)c$$

and so

$$k = \frac{\alpha^2 c}{1 - \alpha} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (ii.)$$

In his original development of this equation Ostwald (1888) assumed that  $\alpha$  was equal to the conductance ratio, that is to the ratio of the equivalent conductance at the concentration  $c$  to the value at infinite dilution ( $\alpha = \Lambda_c/\Lambda_o$ ), and found that weak acids and bases satisfied the requirements of the mass action equation. With strong acids and bases and all salts, that is, with strong electrolytes, the value of the quantity  $\alpha^2 c/(1 - \alpha)$  was by no means constant and independent of the concentration of the solution. From time to time various formulæ were suggested which related the degree of dissociation  $\alpha$ , or more correctly the conductance ratio, with the concentration of a solution of a strong electrolyte; most of these were empirical, and although some were of a semi-theoretical nature they all failed to represent adequately the behaviour of strong electrolytes.



**The Conductance Ratio.** The failure of the Ostwald (Dilution Law) equation may be attributed to two main factors: in the first place the conductance ratio may not be equal to the degree of dissociation. The relationship  $\alpha = \Lambda_c/\Lambda_o$  involves the assumption that the speeds of the ions remain constant at all concentrations; if the oppositely charged ions exert any appreciable attraction for one another it is very improbable that the velocities will be independent of the proximity of the ions to one another, and consequently of their concentration. It will be seen later that according to modern theories almost the whole of the change in the equivalent conductance with change of concentration is to be attributed to differences in the ionic velocities rather than to any marked variation in the degree of dissociation. This subject will be discussed more fully subsequently.

### THE ACTIVITY CONCEPT

The second factor to be considered is that even if the true degree of dissociation were known the concentrations determined in this manner may not necessarily represent the "active masses" required by the law of mass action. This was realised several years ago (1900) and formulæ were suggested to allow for the reduction in effective concentration resulting from interactions between the ions themselves and between ions and molecules. The equations involved a number of empirical coefficients, and did not meet with any success. In 1908, however, G. N. Lewis introduced the concept of "activity," which forms the basis of the modern treatment of strong electrolytes.

If  $\Delta F$  represents the change of free energy when one gm. mol. of any ion or compound is transferred from a solution in which its concentration is  $c_1$  to one in which the concentration is  $c_2$ , then

$$-\Delta F = RT \ln \frac{a_1}{a_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (iii.)$$

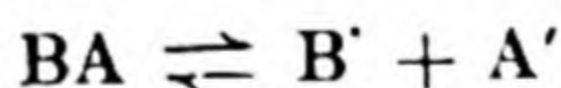
where  $a_1$  and  $a_2$  are the corresponding activities. If the concentration terms  $c_1$  and  $c_2$  satisfied exactly the requirements of



the gas law equation in the form  $P = RTc$ , then it can be shown by thermodynamics that

$$-\Delta F = RT \ln \frac{c_1}{c_2}; \quad . . . . . (iv.)$$

hence the ratio of the activities  $a_1/a_2$  actually represents the ratio of the *ideal* concentrations which satisfy the gas laws. When the measured, or stoichiometrical, concentration of any component obeys the ideal solution laws, then the concentration ( $c$ ) and activity ( $a$ ) may be put equal to one another; this is rarely the case, however, except at infinite dilution, and as a general rule  $a$  and  $c$  are different, the former representing the ideal concentration and the latter the actual value. The ratio of activity to concentration,  $a/c$ , is called the "activity coefficient"; it may be regarded as a measure of the extent to which a molecule or an ion approaches ideal behaviour. By a simple thermodynamic treatment it may be deduced that any concentration term satisfying the gas law equation can be inserted with complete accuracy in the law of mass action equation for an equilibrium constant; it follows, therefore, that the ideal concentration, or activity, should always be used in applications of the law of mass action. The use of activity to represent the "ideal" concentration applies to weak electrolytes and to non-electrolytes, as well as to strong electrolytes. Returning to the equilibrium



the accurate expression applicable under all conditions is

$$K = \frac{a_{B'} \times a_{A'}}{a_{BA}} \quad . . . . . (v.)$$

where the  $a$  terms represent the activities of the respective species.

For weak electrolytes the conductance ratio is probably a satisfactory measure of the degree of dissociation, and at the same time the activities and concentrations of the various ions and undissociated molecules are almost identical. Under these conditions the exact equation (v.) can be reduced to the form (equation (i.)) in which Ostwald applied the law of mass action, and it is not surprising that satisfactory results were obtained for



weak electrolytes. With strong electrolytes, however, not only does the conductance ratio fail to give a true indication of the degree of dissociation, but the activity may differ markedly from the concentration especially in concentrated solutions.

In the early development of the activity concept the quantities were determined in a purely empirical manner as the ideal concentrations which complied with the requirements of the gas laws or of the law of mass action; hence the activities appeared to have no special importance, and as a result the whole concept met with much criticism. In recent years, however, it has been found possible to calculate activities, at least in dilute solutions of electrolytes, on purely theoretical grounds, and so these quantities are beginning to acquire a definite physical significance. It must be admitted, however, at the outset that if this calculation is to be entirely free from empirical quantities it can only be applied to very dilute solutions, so much so that Bancroft (1926) has referred to them as "slightly polluted water." In spite of his criticism it will be seen in later sections of this chapter that results of considerable importance and interest have followed from the theoretical treatment of the activity problem.

Before discussing the modern theory of electrolytes reference must be made to the experimental methods available for the determination of activities. Since these quantities are really relative (cf. equation (iii.)), numerical values can only be obtained with reference to a standard state; the actual standard chosen may vary in different instances, but in connection with the study of strong electrolytes the activity of a solute at infinite dilution is defined as equal to its concentration under the same conditions. The concentration may be expressed in terms of molality ( $m$ ), defined as the number of gm. mols. of solute per 1,000 gms. of solvent, or of volume concentration ( $c$ ), *i.e.*, gm. mols. per litre, or of the molar fraction. It follows, therefore, that the activity coefficient is unity at infinite dilution, when activity and concentration are equal, but at all finite concentrations the activity coefficient is in general not unity, and, as already stated, represents the approach to ideal behaviour. In the thermodynamic treatment of activity coefficients developed by Lewis and Randall



(1921) the concentration of any particular ionic species is taken as the *total* possible molality, *i.e.*, the stoichiometric concentration, without any allowance being made for incomplete dissociation of the electrolyte. This stoichiometric activity coefficient is generally represented by the symbol  $\gamma$ ; it includes a factor for any deviation from complete ionisation. When considering the application of the law of mass action to electrolytic equilibria it is more convenient to employ an activity coefficient  $f$  involving the *actual* concentration of an ion, as distinct from its total possible concentration. If the dissociation of a strong electrolyte is considered to be complete, or almost so, as in the modern theory of electrolytic dissociation, then the values of  $f$  and  $\gamma$  must be identical; in dilute solutions the two quantities cannot differ appreciably, even if dissociation is not quite complete. The possible difference between the two methods of expressing activity coefficients must, however, be borne in mind.

For a uni-univalent electrolyte, *e.g.*, potassium chloride, of the general formula BA, the activities of the positive ( $B'$ ) and negative ( $A'$ ) ions may be represented by  $a_+$  and  $a_-$  respectively, whereas  $a_2$  is the activity of the undissociated molecules, then

$$\frac{a_+ a_-}{a_2} = K \quad \dots \quad (vi.)$$

Since the activities must comply with the law of mass action this equation is strictly applicable to all classes of electrolytes. The mean activity  $a_{\pm}$  of the two ions is taken as the geometric mean of the separate activities, thus

$$a_{\pm} = \sqrt{a_+ a_-} = \sqrt{K a_2} \quad \dots \quad (vii.)$$

The activity coefficients of the separate ions are  $a_+/c_+$  and  $a_-/c_-$ , where  $c_+$  and  $c_-$  are the concentrations of the individual ions; the activity coefficient  $\gamma$  of the electrolyte is defined as the geometric mean of the separate activity coefficients, thus

$$\gamma = \sqrt{\gamma_+ \gamma_-} = \sqrt{\frac{a_+}{c_+} \cdot \frac{a_-}{c_-}} = \frac{a_{\pm}}{c_{\pm}} \quad \dots \quad (viii.)$$

where  $c_{\pm}$  is the mean concentration of the two ions; for a solution of a single uni-univalent electrolyte  $c_{\pm}$  is equal to  $c$ .



## DETERMINATION OF ACTIVITY COEFFICIENTS

**The Freezing-point Method.** It can be deduced thermodynamically that for an aqueous solution

$$d \ln a_2 = \frac{d\theta}{\lambda c} + 0.00057 \frac{\theta}{c} \frac{d\theta}{c} \quad . \quad . \quad . \quad (ix.)$$

where  $a_2$  is the activity of the solute,  $c$  is the concentration of the solution,  $\theta$  the lowering of the freezing point from that of the pure solvent, and  $\lambda$  is the molar lowering of freezing point at infinite dilution; the heat of dilution is ignored in this deduction. For a dilute solution the last term of the equation is very small and may be neglected; hence

$$d \ln a_2 = \frac{d\theta}{\lambda c} \quad . \quad . \quad . \quad . \quad . \quad (ix. a)$$

Substituting for  $a_2$  an equivalent term obtained from equation (vii.) it is found that for a uni-univalent electrolyte

$$d \ln a_{\pm} = \frac{d\theta}{2\lambda c}; \quad . \quad . \quad . \quad . \quad . \quad (x.)$$

for an electrolyte dissociating into  $\nu$  ions the integer 2 on the right-hand side of this equation is replaced by  $\nu$ . Subtracting  $d \ln c$  from the left-hand side and  $dc/c$ , to which it is equal, from the right-hand side of equation (x.) there results

$$d \ln \frac{a_{\pm}}{c} = d \ln \gamma = \frac{d\theta}{2\lambda c} - \frac{dc}{c} \quad . \quad . \quad . \quad (xi.)$$

In order to integrate this expression,\* and so obtain an equation for  $\gamma$ , or  $\ln \gamma$ , it is necessary to find a connection between  $\theta$  and  $c$ ; no theoretical relationship is obtainable from thermodynamics, but Lewis and Linhart (1919) found empirically that

$$1 - \frac{\theta}{2\lambda c} = \beta c^a \quad . \quad . \quad . \quad . \quad (xii.)$$

for dilute solutions of electrolytes, where  $a$  and  $\beta$  are constants which can be determined from measurements of freezing-point depressions. By differentiating equation (xii.) a value for  $d\theta$  is

\* Graphical methods may also be used, but these are tedious.







TABLE LXIV.—Mean Activity Coefficients from Freezing-Point Data

Electrolyte.	Molar Concentration.						
	0.0001	0.0005	0.001	0.005	0.01	0.05	0.1
HCl .	0.992	0.981	0.973	0.940	0.916	0.840	0.809
NaCl .	0.985	0.972	0.963	0.928	0.906	0.834	0.792
KCl .	0.982	0.970	0.961	0.926	0.903	0.821	0.779
KNO <sub>3</sub> .	0.994	0.984	0.976	0.943	0.916	0.806	0.732
K <sub>2</sub> SO <sub>4</sub> .	0.935	0.885	0.85	0.75	0.69	0.505	0.421
BaCl <sub>2</sub> .	0.94	0.89	0.865	0.77	0.72	0.568	0.501
Pb(NO <sub>3</sub> ) <sub>2</sub> .	0.965	0.922	0.891	0.773	0.694	0.465	0.369
CuSO <sub>4</sub> .	0.85	0.75	0.69	0.50	0.40	0.216	0.158
La(NO <sub>3</sub> ) <sub>3</sub> .	0.92	0.85	0.81	0.66	0.57	0.391	0.326

$c$  is the concentration and  $\gamma$  the activity coefficient, it follows that

$$(c_+\gamma_+)(c_-\gamma_-) = K_s \quad \dots \quad (\text{xv.})$$

where  $c_+$  and  $c_-$  are the ionic concentrations; this equation always holds irrespective of the presence of common or other ions. Since  $c_+c_-$  is equal to  $c_{\pm}^2$  (equation (vii.)) and  $\gamma_+\gamma_-$  is equal to  $\gamma_{\pm}^2$  (equation (viii.)) then

$$c_{\pm}\gamma_{\pm} = \sqrt{K_s} \quad \dots \quad (\text{xvi.})$$

and

$$\gamma_{\pm} = \sqrt{K_s}/c_{\pm} \quad \dots \quad (\text{xvii.})$$

If the activity coefficient and the solubility ( $S$ ) of a sparingly soluble salt, in the absence of any other electrolyte, are known,  $K_s$  may be calculated, since under these conditions  $c_{\pm}$  is equal to  $S$ . Alternatively  $K_s$  may be determined by plotting the value of  $c_{\pm}$ , in the presence of various salts, against a suitable function of the total ionic concentration; the curve may be extrapolated to zero concentration when  $\gamma_{\pm}$  is unity, and  $c_{\pm}$  is then equal to  $\sqrt{K_s}$ , (equation (xvi.)). From a knowledge of  $K_s$  it is possible to calculate the activity coefficient  $\gamma_{\pm}$  of a sparingly soluble salt in the presence of other salts, provided the solubility of the former may be determined.

The published data on the solubility of thallous chloride have







TABLE LXV.—*Activity Coefficients of Thallous Chloride at 25° (in the Presence of Other Electrolytes)*

Total Concentration.	Nature of Electrolyte.				
	KNO <sub>3</sub>	KCl	HCl	TlNO <sub>3</sub>	Tl <sub>2</sub> SO <sub>4</sub>
*0.01N . . .	0.909	0.909	0.909	0.909	0.909
0.02 . . .	0.872	0.871	0.871	0.869	0.860
0.05 . . .	0.809	0.797	0.798	0.784	0.726
0.1 . . .	0.742	0.715	0.718	0.686	0.643
0.2 . . .	0.676	0.613	0.630	0.546	—

Thus in a solution of 0.1 molar hydrochloric acid and 0.5 molar barium chloride, for example, the ionic strength is given by

$$\mu = \frac{1}{2} \{ 0.1 \text{ (for H')} + 1.1 \text{ (for Cl')} + 0.5 \times 2^2 \text{ (for Ba'')} \} = 1.6.$$

If the values of the activity coefficients of thallous chloride (Table LXV.) are plotted against the ionic strengths of the solutions, it is found that the curves for the various electrolytes approach one another closely, especially in solutions below 0.05 molar. These results favour the empirical rule of Lewis and Randall that the activity coefficient is a function of the ionic strength only. It has been suggested by Davies and his co-workers (1930 *et seq.*) that if an appropriate allowance be made for the incomplete dissociation of the added electrolytes in the more concentrated solutions, the activity coefficient of a sparingly soluble salt remains independent of the nature of that electrolyte up to ionic strengths of 0.5 ; in still more concentrated solutions each added electrolyte exerts its own specific influence.

**The Electromotive Force Method.** The *E.M.F.* of a reversible concentration cell is a measure of the free energy of transfer of electrolyte from a solution at one concentration to another at a different concentration ; the exact formula for the *E.M.F.* should thus involve activities in place of concentration terms. For example, the *E.M.F.* of the cell  $\text{H}_2 (1 \text{ atm.}) / \text{HCl aq. } (c_1) \text{ MCl} / \text{M} / \text{MCl}$

• Activity coefficients obtained by extrapolation.







TABLE LXVI.—*Activity Coefficients from E.M.F. Measurements (25°)*

<i>c.</i>	HCl.	NaCl.	KCl.	KBr.	KI.	H <sub>2</sub> SO <sub>4</sub> .	NaOH.	KOH.
0.001	0.965	0.966	0.965	—	—	—	—	0.989
0.005	0.929	0.928	0.926	—	—	—	—	0.954
0.01	0.904	0.903	0.899	—	—	0.617	0.902	0.920
0.05	0.881	0.821	0.815	0.816	0.820	0.397	0.825	0.822
0.1	0.976	0.778	0.764	0.765	0.775	0.313	0.775	0.789
0.5	0.757	0.678	0.644	0.653	0.678	0.178	0.702	0.750
1.0	0.810	0.658	0.597	0.612	0.649	0.150	0.680	0.760
2.0	—	0.670	0.569	0.589	0.646	0.147	0.743	—
8.0	—	0.714	0.571	0.590	—	0.166	0.888	1.062

extend to activities, although it is probable that in dilute solutions the activities of the two ions will be identical if they are of the same valency type. At infinite dilution the activity coefficients of all ions are unity, but at appreciable concentrations the deviations from unity may vary with the nature of the ion.

Theoretically, individual ion activities should be determinable by a method based on measurements of the *E.M.F.*'s of certain cells, but there are difficulties, connected with liquid junction potentials, which make the method inaccurate. An alternative procedure has been proposed as follows. In dilute solutions of univalent chlorides the product of the transport number of the chlorine ion and the equivalent conductance of the solution, at a given concentration, is found to be independent of the nature of the cation. This indicates that in a dilute solution the chlorine ion contributes a definite amount towards the conductance of a chloride solution, irrespective of the nature of the other ion. Further, the mean activity of a given chloride in dilute solution depends only on the ionic strength (p. 446); hence it is reasonable to assume that the activity of the chlorine ion is constant in dilute solutions of different chlorides at the same molar concentrations. This independence of conductance and activity of a given ion of the nature of the other ions is considered to apply to all ions. It has also been supposed (MacInnes, 1921), on the basis of similarity of weight and mobility of the potassium and chlorine ions, that in



a dilute solution of potassium chloride the two ions have the same activities. For potassium chloride of ionic strength 0.01, Lewis and Randall take  $\gamma$  as 0.922; hence in accordance with the views expressed the activity coefficient of potassium and chlorine ions in *any solution* of ionic strength 0.01 is 0.922. The mean activity of potassium iodate at  $\mu = 0.01$  is 0.882, and so the activity of the iodate ion can be found to be 0.844 at this ionic strength. In the same manner the individual ionic activities of the other ions may be determined; unfortunately there is no method of verifying these values.

In addition to the methods described here for obtaining the activity coefficients of electrolytes others are available, but sufficient has been said to indicate the most important procedures used for their *empirical* determination; the attempt to find a theoretical basis for these quantities will now be discussed.

### THE MODERN DISSOCIATION THEORY

It is generally accepted at the present time that strong electrolytes are almost *completely ionised* at all dilutions; this view had been put forward tentatively by various writers, from 1904 onwards, but it was not until recent years that developments in the field of X-ray crystallography and in the electronic theory of valency made the theory appear plausible. From the X-ray examination of crystals of alkali halides it was concluded, and subsequently confirmed by a study of other salts, that the molecule is not the unit of structure in the crystal lattice.

A sodium chloride crystal consists of a face-centred cubic sodium lattice and a face-centred cubic chlorine lattice, but there is no evidence of a sodium chloride molecule lattice. It is very improbable that actual atoms of sodium and cf. chlorine are present in the lattice, but the corresponding *ions* may very well be the units of the crystal structure. This idea is in harmony with those based on the electronic theory of valency (Chapter I.), according to which a salt consists of two separate *ions* held together by electrostatic forces. There is very little doubt, therefore, that in a solid salt ionisation is complete, but the



conducting power of a crystal is small, since free movement of the ions is prevented by the strong forces inside the crystal lattice. On dissolving the salt in water, or by melting it, the ions are able to move relative to one another and so conduct an electric current. The electrostatic attractions between ions must, presumably, still be operative in solution, especially if the latter is concentrated. These attractions may result in a definite pairing of ions, or in a continual interchange of partners, but the net result will be equivalent to *partial dissociation, although ionisation may be complete*. In dilute solution, however, the ions will be comparatively far apart and inter-ionic attractions negligible; the condition will then correspond with complete dissociation. The theory is so far in qualitative agreement with the behaviour of strong electrolytes, and provides a ready explanation for the fact that the simple form of the Ostwald dilution law (equation (ii.), p. 488) is not applicable to such solutions.

**Milner's Theory.** The first quantitative application of the theory of complete ionisation was made by Milner (1912), who was led to reject the older views by the complete failure of the law of mass action to apply to strong electrolytes. He considered that in such solutions ionisation was complete, but that the deviation from ideal behaviour was accounted for by the electrostatic attraction between the charged particles. By assuming that the Clausius "virial" equation, which allowed for the deviation of gases from the perfect gas laws in terms of the molecular attractions, applied to electrolytic solutions, Milner was able to calculate the difference between the theoretical and actual osmotic effects, *e.g.*, depression of the freezing point, for a number of uni-univalent salts at various concentrations. The results obtained were in excellent agreement with the experimental observations for sodium and potassium chlorides, and in general agreement with those for ammonium chloride and various nitrates. Owing to the very complicated mathematical and arithmetical treatment involved in Milner's deductions, his extremely important work did not receive the attention which it merited; incidentally the theory was put forward before the scientific world was prepared for the change from partial to complete ionisation.



In 1918 the idea of complete dissociation was revived by Ghosh, whose theory met with a great deal of approval when it was first proposed ; owing to the improbabilities involved in its postulates it soon fell into disrepute, and will receive no more than a passing mention here.

### THE DEBYE-HÜCKEL THEORY

In 1923 Debye and Hückel developed the inter-ionic attraction theory of Milner in a more direct form. The fundamental idea underlying the treatment is that owing to electrical attractions between positive and negative ions there are, on the average, in the neighbourhood of any ion more ions of unlike than of like sign ; consequently when a solution is diluted the separation of the ions involves doing internal work against this electrostatic attraction in addition to the purely osmotic work of dilution. The theory, therefore, assumes complete ionisation and attributes deviations from ideal behaviour to the inter-ionic attractions. The original development of the Debye-Hückel theory is highly mathematical ; the simpler presentation of the theory by Noyes (1924) will be followed here.

By assuming that the Boltzmann principle of the distribution of molecules in a region of varying field of force applies to ions existing in a space of varying electrical potential due to their own attractions and repulsions, the distribution of positive and negative ions in the vicinity of a given ion can be determined. From this distribution the density of electricity, *i.e.*, total charge per unit volume, at a given distance from a central ion, may be calculated, and then by means of Poisson's equation of electrostatics the electrical potential at this distance can be evaluated. The resulting expression may be divided into two terms : one representing the potential due to the central ion if there were no surrounding ions, and the other is equivalent to the potential arising from the unequal distribution of positive and negative charges in the surrounding "ion atmosphere." When the distance from the central ion is zero the latter term gives the potential *at the ion itself* produced by the excess of oppositely charged ions in



its vicinity ; multiplying this potential by the ionic charge gives the total energy required to remove the ion from its electrical atmosphere. If the dimensions of the ion may be neglected, that is for a point charge, this energy term is

$$\frac{z^2 \epsilon^2 \kappa}{D} \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \quad (\text{xx.})$$

where  $z$  is the valency of the ion,  $e$  is the electronic charge ( $ze$  is the charge on the ion),  $D$  is the dielectric constant of the medium, and

$$\kappa \equiv \sqrt{\frac{4\pi\epsilon^2 \Sigma(cz^2)}{1000 DRT}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (\text{xxi.})$$

$c$  being the concentration of the ions of valency  $z$ , in gm. ions per litre, and  $R$  is the gas constant. The quantity  $1/\kappa$  has the dimensions of a distance, and is sometimes called the radius of the ion atmosphere, since it represents the radius of a sphere on the surface of which the uniform distribution of a charge  $ze$  would have the same effect as the ion atmosphere. In order to find the total energy required to remove all the ions of a particular kind formed by 1 gm. mol. of electrolyte from their respective ion atmospheres, the energy term (xx.) must be multiplied by  $N\nu$ , where  $N$  is the Avogadro number, and  $\nu$  is the number of ions of that kind produced by a molecule of electrolyte on dissociation; this is given by the expression

$$\frac{N\epsilon^2\kappa \cdot v z^2}{D} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (\text{x x i i .})$$

If *all* the ions in the electrolyte are removed at the same time from their respective ion atmospheres, this term must be summed for all the different kinds of ions present, and then divided by two, otherwise the work required to separate any pair of ions will be counted twice. Since the energy effects for the different ions are additive, this total may be distributed amongst the different kinds of ions, and so the contribution of each kind is found to be

$$\frac{N\epsilon^2\kappa \cdot v_z^2}{2D} \quad . \quad . \quad . \quad . \quad . \quad . \quad (\text{xxiii.})$$

**This quantity also represents the share of the particular ion in**



the energy change attending the *dilution* of a solution containing 1 gm. mol. of completely ionised electrolyte, to such an extent that the ions are too far apart to exert any mutual electrostatic attraction. Noyes has shown that this is two-thirds of the energy change attending the *transfer* of the ions from an infinite volume of solution at the given concentration to an infinite volume of extremely dilute solution; hence the total energy change of transfer, *at constant volume*, is given by

$$\Delta H = \frac{8}{2} \cdot \frac{N\epsilon^2\kappa}{2D} \cdot \nu z^2 \quad \dots \quad (xxiv.)$$

This total energy change may be related to the free energy change ( $\Delta F$ ) by a modified form of the Gibbs-Helmholtz equation

$$d\left(-\frac{\Delta F}{T}\right) = \frac{\Delta H}{T^2} \cdot dT \quad \dots \quad (xxv.)$$

whence it follows that

$$d\left(-\frac{\Delta F}{T}\right) = \frac{8}{2} \cdot \frac{N\epsilon^2\kappa}{2DT^2} \cdot \nu z^2 \cdot dT \quad \dots \quad (xxvi.)$$

If the dielectric constant is assumed to be independent of temperature, then it is found on integrating equation (xxvi.) that

$$-\Delta F = IT - \frac{N\epsilon^2\kappa}{2D} \cdot \nu z^2; \quad \dots \quad (xxvii.)$$

it should be noted on integration that the term for  $\kappa$  involves  $T^{-0.5}$ . The integration constant  $I$  may be evaluated by realising that in an ideal solution the electrostatic effects expressed by the second term on the right-hand side of equation (xxvii.) become zero; hence  $IT$  represents the ideal value of the free energy of transfer of the  $\nu$  gm. ions produced by the ionisation of 1 gm. mol. of electrolyte. This *ideal* value is given by

$$\nu RT \ln c/c_0 \quad \dots \quad (xxviii.)$$

where  $c$  and  $c_0$  represent the concentrations before and after the transfer. The actual free energy for a non-ideal solution, corrected for electrostatic attractions, is then

$$-\Delta F = \nu RT \ln \frac{c}{c_0} - \frac{N\epsilon^2\kappa}{2D} \cdot \nu z^2 \quad \dots \quad (xxix.)$$



Alternatively the free energy change resulting from the transfer of  $\nu$  gm. ions from a solution of concentration  $c$ , in which the activity of the particular ions is  $a$ , to one of concentration  $c_0$  and activity  $a_0$ , is

$$-\Delta F = \nu RT \ln \frac{a}{a_0} = \nu RT \ln \frac{cf}{c_0 f_0} \quad . \quad . \quad . \quad (\text{xxx.})$$

where  $f$  and  $f_0$  represent the corresponding activity coefficients. (Since the theory under discussion postulates complete ionisation the coefficient  $f$  is used instead of  $\gamma$ .) The solution  $c_0$  is supposed to be extremely dilute, and so  $f_0$  may be taken as unity, and hence on comparing equations (xxix.) and (xxx.) it is seen that

$$\ln f = -\frac{N\epsilon^2\kappa z^2}{2DRT} \quad . \quad . \quad . \quad (\text{xxxi.})$$

Substituting for  $\kappa$  (equation (xxi.)), and reducing natural logarithms to those with a base of 10, it is found that

$$-\log f = \left( \frac{N\epsilon^3\sqrt{\pi/1000}}{2.302 R^{1.5}} \right) \frac{z^2\sqrt{\Sigma(cz^2)}}{(DT)^{1.5}} \quad . \quad . \quad (\text{xxxii.})$$

$$= \frac{A'z^2\sqrt{\Sigma(cz^2)}}{(DT)^{1.5}} \quad . \quad . \quad . \quad (\text{xxxiii.})$$

where  $A$  is a universal constant equal to the first term, in the brackets, on the right-hand side of equation (xxxii.). The quantity  $\Sigma(cz^2)$  is obviously equal to twice the ionic strength (equation (xviii.), p. 446), *i.e.*,  $2\mu$ , and so

$$-\log f = \frac{Az^2\sqrt{\mu}}{(DT)^{1.5}} \quad . \quad . \quad . \quad (\text{xxxiii. } a)$$

where  $A$  is equal to  $A'\sqrt{2}$ . For water as solvent  $D$  is 87.8 at  $0^\circ$ , and 78.8 at  $25^\circ$ ; substituting these values, and the known values of  $N$ ,  $\epsilon$ ,  $R$  and  $\pi$ , it is found that in aqueous solution

$$-\log f = 0.487 z^2\sqrt{\mu} \text{ at } 0^\circ \quad . \quad . \quad (\text{xxxiv. } a)$$

or

$$0.505 z^2\sqrt{\mu} \text{ at } 25^\circ \quad . \quad . \quad (\text{xxxiv. } b)$$

These equations show that there is a theoretical basis for the empirical discovery of Lewis and Randall that the activity coefficient of a given ion depends only on the ionic strength of



the solution ; incidentally they agree with the observation already made that the coefficients are related to the valency of the ions (p. 444).

In deducing these equations two important assumptions have been made : firstly, that the ions are infinitely small, and secondly, that the dielectric constant of the medium is independent of temperature. It has been shown, however, that by a somewhat modified treatment the same equations may be deduced without making the latter assumption. In order to correct for the size of the ions it can be demonstrated that the value obtained for the work required to move an ion from its ion atmosphere must be multiplied by  $1/(1 + \kappa a)$ , where  $\kappa$  has the same significance as previously, and  $a$  is the average " effective diameter " of the ions ; the latter may be regarded as the mean distance up to which any ion can approach a given ion, and probably includes the dimensions of a sheath of solvent molecules. Hence

$$-\log f = \frac{Az^2\sqrt{\mu}}{(DT)^{1.5}} \cdot \frac{1}{1 + \kappa a} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (xxxv.)$$

For a given solvent at a definite temperature  $\kappa$  is proportional to  $\sqrt{\Sigma (cz^2)}$ , and hence to  $\sqrt{\mu}$ , and so it follows that

$$-\log f = \frac{Az^2\sqrt{\mu}}{1 + aB\sqrt{\mu}} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (xxxvi.)$$

where  $B$  is made up of known constants, and for water is found to be  $3.3 \times 10^7$  at ordinary temperatures.

Hückel (1925) has shown that the electrolyte produces a change of dielectric constant in the vicinity of an ion, and by assuming  $D$  to be a linear function of the concentration, it has been deduced that a correction, approximately proportional to the ionic strength, must be introduced, giving

$$-\log f = \frac{Az^2\sqrt{\mu}}{1 + aB\sqrt{\mu}} - C\mu \quad \cdot \quad \cdot \quad \cdot \quad (xxxvii.)$$

This equation gives the activity coefficient of an ion of valency  $z$ , but the (geometric) mean activity coefficient  $f_{\pm}$  of the salt consisting of two kinds of ions may be readily shown to be given by



$$-\log f_{\pm} = \frac{z_+ z_- A \sqrt{\mu}}{1 + aB \sqrt{\mu}} - C\mu \quad . \quad . \quad . \quad (\text{xxxviii.})$$

where  $A$  and  $B$  are, the same as before, constants for the given solvent at a definite temperature, and  $a$  and  $C$  are constants for the solute. Sometimes this equation is written, after Brønsted, in the form

$$-\log f_{\pm} = z_+ z_- A \sqrt{\mu} - b\mu \quad . \quad . \quad . \quad (\text{xxxix.})$$

the constant  $b$  for the given solution being related to  $a$ ,  $A$ ,  $B$  and  $C$ .

Equation (xxxviii.) may be regarded as the final form of the Debye-Hückel expression for strong electrolytes; it attempts to give a quantitative value for the activity coefficient of a salt at different ionic strengths. In dilute solution it is clear that the second term on the right-hand side may be neglected, and the resulting equation indicates that the activity coefficient decreases with increasing ionic strength; in more concentrated solutions the term  $C\mu$  will become appreciable, and the activity coefficient will commence to increase, as is actually found to be the case (Table LXVI.). In order to test the quantitative accuracy of the Debye-Hückel equation it is necessary to know  $a$ , the mean ionic diameter, and  $C$  for a given electrolyte, but there is yet no method by means of which they may be calculated without reference to experimental activity data. It is only in *very dilute solution*, therefore, when these constants may be neglected, and the equation reduces to the form

$$-\log f_{\pm} = z_+ z_- A \sqrt{\mu} \quad . \quad . \quad . \quad . \quad (\text{xl.})$$

that it may be unequivocally verified. For an electrolyte in water at  $25^\circ$ , the limiting equation approached at high dilution should be

$$-\log f_{\pm} = 0.505 z_+ z_- \sqrt{\mu} \quad . \quad . \quad . \quad . \quad (\text{xl. a})$$

## TESTS OF THE DEBYE-HÜCKEL THEORY.

**Solubility.** It has been shown (p. 445) that for a saturated solution of a sparingly soluble uni-univalent salt, replacing  $\gamma$  by  $f$  since dissociation is assumed to be complete,

$$c_{\pm} f_{\pm} = \sqrt{K}, \quad . \quad . \quad . \quad . \quad (\text{xvi. a})$$



If  $S_0$  is the solubility of the salt in pure water, and  $S$  the value in the presence of any other electrolyte not containing a common ion, then

$$S_0 f_0 = S f = \sqrt{K_s},$$

$$\therefore \log \frac{S}{S_0} = \log f_0 - \log f \quad . \quad . \quad . \quad (xli.)$$

According to the Debye-Hückel theory for dilute solutions

$$-\log f_0 = Az_+ z_- \sqrt{\mu_0} \text{ and } -\log f = Az_+ z_- \sqrt{\mu}$$

where  $\mu_0$  and  $\mu$  are the ionic strengths of the solutions containing the salt only and one containing added electrolytes, respectively; hence

$$\log \frac{S}{S_0} = Az_+ z_- (\sqrt{\mu} - \sqrt{\mu_0}) \quad . \quad . \quad . \quad (xlii.)$$

It follows, therefore, that if  $\log S/S_0$  is plotted against  $\sqrt{\mu}$  for a given saturating salt, since  $\mu_0$  is constant the *limiting slope* of the curve in dilute solution should be  $Az_+ z_-$ , *irrespective of the nature of the added electrolytes*. This conclusion has been tested by old and new experimental data; the slopes of the curves were certainly proportional to the product of the valencies of the ions of the saturating salt ( $z_+ z_-$ ), but the value of  $A$  was sometimes lower than that required by the Debye-Hückel theory. Marked deviations from the theoretical curve have been observed when the saturating salt has an ion of high valency, and the added salts have high valency ions of opposite sign; for example, the solubility of lanthanum iodate is abnormal in the presence of sulphates, although the results with chlorides and nitrates are in agreement with the Debye-Hückel theory. These deviations are probably connected with the neglect of certain terms in the development of the expression for the electrical density in the vicinity of an ion (*vide infra*). General agreement with the theoretical requirements is also shown by solubility values in non-aqueous solvents, *e.g.*, acetone, and methyl and ethyl alcohols.

**Osmotic Properties.** Activity coefficients from freezing-point measurements are generally in good agreement with the values calculated from the Debye-Hückel equation for very dilute



solutions. Although the limiting equation is of the right form, the constant  $A$  for water at  $0^\circ$  was found to be 0.39 to 0.46, rather than 0.487 (equation (xxxiv. a)). If allowance is made for the size of the ions, by putting  $a = 1 - 3 \times 10^{-8}$  cm. (equation (xxxvi.)), the extended Debye-Hückel equation can be made to represent actual observations in a satisfactory manner. Freezing-point determinations have also been made in liquid ammonia ( $D = 25.1$ ;  $T = -75^\circ$ ), acetic acid ( $D = 7$ ,  $T = 16.6^\circ$ ) and cyclohexanol ( $D = 15$ ,  $T = 24^\circ$ ), and activity coefficients determined from boiling-point elevations in methyl and ethyl alcohols ( $D = 22.7$  and  $18.7$  respectively) and in acetone ( $D = 21$ ); the results all comply with the limiting requirements of the Debye-Hückel theory.

**E.M.F. Measurements.** The activity coefficients of various electrolytes calculated from *E.M.F.* measurements are in general agreement with the requirements of equation (xl.) in dilute solutions, but the value of  $A$ , particularly in non-aqueous solutions, is often smaller than the theoretical figure. Measurements have been made in aqueous and aqueous-alcoholic solutions, as well as in methyl and ethyl alcoholic solutions, and also in aqueous electrolytes containing glycerol and sucrose; the results are generally in harmony with the Debye-Hückel equation.

**Heat of Dilution.** Since the total energy required to remove an ion from its electrical atmosphere does not depend on the specific nature of the ion, but only on its electrical charge and environment, the heat of dilution of different salts of the same valency type should be the same for a given ionic strength. In view of the assumptions involved in the development of the theory of complete ionisation, this result would only be expected for dilute solutions. Recent experiments (Lange, 1927 *et seq.*) seem to bear out the essential dependence of heat of dilution on valency type and ionic strength.

**Viscosity and Partial Molal Volume.** It has been shown that the application of the inter-ionic attraction theory leads to the expectation that both the viscosity (Falkenhagen and Dole, 1929) and the partial molal volume (Redlich, 1931) of a dilute solution should be linear functions of the square-root of the concentration;



these relationships have been verified by a number of investigators. The calculated constants of the equations are often in excellent agreement with the experimental values.

**Modifications of the Theory.** In the original calculation by Debye and Hückel of the potential due to the ionic atmosphere (p. 452), the value of the ionic radius is supposed to be very small, that is, practically a point charge is considered, so that in the development of an exponential expression all terms beyond the first in the series may be neglected. Gronwall, La Mer and Sandved (1928), without introducing any new principle, have given a more complete solution of the expression which is applicable to ions of appreciable size, for an electrolyte having ions of the same valency, *i.e.*, of symmetrical valence type. The resulting equation for the activity coefficient, although much more cumbersome, is claimed to be in better agreement with the observations than is the ordinary Debye-Hückel formula. La Mer, Gronwall and Greiff (1931) have extended the mathematical development to salts of unsymmetrical valence type, and have found the resulting equations to be more suited to the representation of *E.M.F.*, freezing-point and solubility data than is the Debye-Hückel equation even in its extended form (equation xxxviii.); the former expression leads to values of "*a*," the effective ionic diameter, which are much more reasonable than those given by the latter.

Kramers (1927) and Fowler (1927) have pointed out that the Debye-Hückel limiting law must break down, even if allowance is made for the size of the ions, and for higher order terms, when the potential energy of the ions due to their atmospheres becomes comparable with their energy of translation; this will occur more readily the higher the ionic strength of the solution and the lower the dielectric constant. This factor may account for many of the deviations observed, especially with salts of high valency types. Another point of view has been taken up by Bjerrum (1926), to which reference will be made shortly; this author supposes that ions which approach one another more closely than a certain distance are paired in such a way as to be virtually undissociated, and the Debye-Hückel treatment is only applicable to the



remainder. The errors caused by this "ion association" are likely to be greatest for small ions and for media of low dielectric constant.

**Conclusion.** Apart from the limitations mentioned there is no doubt that the Debye-Hückel equation provides in many instances an adequate representation of the behaviour of electrolytic solutions, although, as will be seen later, the fundamental assumption on which it is based, namely, the complete ionisation of salts, is not applicable to all solvents. For dilute solutions in dissociating solvents the simple Debye-Hückel equation is generally applicable as long as the ionic strength does not exceed 0.01, but for more concentrated solutions it is necessary to employ *empirical* values of the mean ionic diameter term "*a*." These values are usually of the correct order of magnitude  $1 - 4 \times 10^{-8}$  cm., and so their use is justified. On the whole it must be concluded that an advance has been made in the direction of finding a physical interpretation of what was at one time a purely empirical quantity, namely, the activity of an ion.

## CONDUCTIVITY AND COMPLETE IONISATION

According to the theories of Milner and Debye and Hückel, every ion in solution is surrounded by an atmosphere in which oppositely charged ions are present in excess; as long as the ion is in stationary equilibrium this atmosphere must have central symmetry. When an electric current is passed through the solution, so that the ion under consideration moves to the right, then during its motion it will constantly have to build up its ion atmosphere to the right, whereas the charge density to the left will die out. If this formation and destruction of the charged atmosphere occurred simultaneously, then there would be no net force of electrical attraction on the moving ion; in actual conduction, however, it is probable that there will be a finite "time of relaxation" during which the right-hand atmosphere is building up to its equilibrium value whilst the left is decaying. Since the ion atmosphere has a charge opposite in sign to that of the moving ion, it follows that there will be an excess of ions of



opposite sign to the left of the moving ion, and these will retard its motion. In the more concentrated solutions the closer packing of the ions will naturally result in a greater decrease of the ionic velocity, and so in spite of complete ionisation the equivalent conductance of the solution must decrease. In order to deduce a connection between conductance and concentration it is necessary to consider, as far as possible, all the forces acting on an ion. The force due to the applied *E.M.F.* is opposed by (a) the electrical attraction resulting from the dissymmetry of the ion atmosphere, and (b) the frictional resistance of the solution, taking into consideration the fact that the applied *E.M.F.* will tend to move the ion atmosphere in a direction *opposite* to that in which the ion is itself moving. When the ion is travelling with a steady velocity these forces balance one another; by combining the formulæ for the different forces, Debye and Hückel (1928) deduced the equation

$$\frac{\Lambda_o - \Lambda_c}{\Lambda_o} = \left[ \frac{1}{8\pi\eta} \cdot \frac{N\epsilon^2}{\Lambda_o} + \frac{\mu_1^2 + \mu_2^2}{2\mu_1\mu_2} \cdot \frac{N\epsilon^2}{6DRT} \right] \kappa \quad . \quad . \quad (\text{xliii.})$$

where  $\eta$  is the viscosity of the solvent,  $\mu_1$  and  $\mu_2$  are the ionic mobilities at infinite dilution, and  $\kappa$  has the same significance as previously. Introducing the appropriate value for the latter (equation (xxi.)) and the known values for the other constants with *water* as solvent, at  $18^\circ$ , it is found that

$$\Lambda_o - \Lambda_c = \left[ 50.2 + 0.385 \Lambda_o \frac{\mu_1^2 + \mu_2^2}{2\mu_1\mu_2} \right] \sqrt{c} \quad . \quad (\text{xliv.})$$

Since  $\mu_1$  and  $\mu_2$  are constant for a given electrolyte, this equation reduces to the form

$$\Lambda_o - \Lambda_c = k\sqrt{c} \quad . \quad . \quad . \quad (\text{xlv.})$$

where  $k$  is a constant; this is identical with the empirical equation suggested many years previously by Kohlrausch, and so is presumably in some agreement with experimental results. The value of  $k$  may be calculated if the ionic mobilities ( $\mu_1$  and  $\mu_2$ ) are known, but the results are not in very good agreement with those observed; thus for potassium chloride the calculated value is 100.2 and the experimental figure is 84.5.

A further theoretical development has been made by Onsager



(1926), who suggested that the Debye-Hückel calculation of the force due to dissymmetry of the ion atmosphere must be modified on account of the natural Brownian movement of the ion. The equation deduced by Onsager for an electrolyte yielding two ions, both having a valency  $z$ , may be written in the form

$$\Lambda_0 - \Lambda_c = \left[ \frac{58.0\sqrt{2}}{(DT)^{1/2}\eta} z^{3/2} + \frac{0.986 \times 10^6}{(DT)^{3/2}} (2\sqrt{2} - 2) \Lambda_0 z^{5/2} \right] \sqrt{c}. \quad (\text{xlvi.})$$

For any uni-univalent electrolyte in *aqueous* solution at  $18^\circ$ , this becomes

$$\Lambda_0 - \Lambda_c = [50.2 + 0.227 \Lambda_0] \sqrt{c} \quad . \quad . \quad (\text{xlvii.})$$

and for potassium chloride,

$$\Lambda_0 - \Lambda_c = 79.7 \sqrt{c} \quad . \quad . \quad . \quad . \quad (\text{xlvi.})$$

This is in better agreement with the experimental results than was the original equation.

In recent years a large number of conductance measurements has been made, particularly in non-aqueous solutions, with the object of testing the Onsager equation. There is little doubt that the curve of  $\Lambda_c$  against  $\sqrt{c}$  becomes linear in all dilute solutions, but the slopes ( $k$ ) of the curves are not always in agreement with the calculated values. It is very probable that other factors have yet to be brought to light in connection with the application of the theory of complete ionisation to conductance problems, but in the meantime the Debye-Hückel-Onsager equation may be accepted as giving the ideal relationship of conductance to concentration. It has, indeed, been suggested that the difference between the observed and calculated values of conductance is due to the fact that either ionisation is not quite complete in solution, or that ions have become "associated" together so as to behave like an undissociated molecule; the ratio of the observed value of  $\Lambda_0$  to the conductance for the same concentration determined from the Onsager equation has been regarded as the true "degree of dissociation" of the electrolyte (Davies, 1927; Hartley, 1929; Martin, 1930; Fuoss and Kraus, 1933). The application of this suggestion has proved to be very fruitful in a number of instances.







minimum, as has been frequently found with solvents of low dielectric constant. It can be seen in a qualitative manner, that as the concentration of an electrolyte increases the extent of ion-association to form pairs will increase, so that the equivalent conductivity diminishes; with increasing concentration, however, triple ions will commence to form, but as these have a resultant charge they will contribute towards the conductivity which consequently commences to rise again. Fuoss and Kraus have shown that for a given electrolyte the conductivity minimum moves towards higher concentrations with increasing dielectric constant of the solvent; with media of high dielectric constant the minimum would occur at unrealisable concentrations, and would, in any case, be much less marked than for solvents with low dielectric constants. The tendency to form triple ions is approximately proportional to  $1/\epsilon^3$ ; this is probably the explanation of the empirical rule discovered by Walden that for a given electrolyte in different media  $\epsilon^3 v_{\text{min.}}$  is a constant, where  $v_{\text{min.}}$  is the dilution at which the conductivity minimum occurs.

### CONDUCTANCES AT HIGH FREQUENCIES AND HIGH VOLTAGES

If a high-frequency alternating voltage is applied to an electrolyte so that the time of oscillation of an ion is equal to, or less than, the "relaxation time," the unsymmetrical charge distribution produced round an ion in motion can no longer form completely; the retardation of the ionic velocity resulting from the dissymmetry of the ion atmosphere thus disappears partially or entirely, and the conductance of the solution should be increased (Debye and Falkenhagen, 1928). The time of relaxation has been calculated to be of the order of  $10^{-10}/c$  sec., where  $c$  is the concentration of the solution; for a 0.001*N*-electrolyte, the time is  $10^{-7}$  sec., and the effect on the conductance of high frequency oscillations with a wavelength of 1 metre (oscillation time  $3.3 \times 10^{-8}$  sec. approx.) should be noticeable. The experimental verification of this forecast was not easy, but distinct evidence in favour of the theory has been obtained by Sack (1928), and others. The effect



should be greater the lower the valencies and mobilities of the ions involved, the higher the dielectric constant of the medium, and the lower the temperature; these points have not yet been subjected to experimental test.

An increase in the conductance of an electrolyte was observed by Wien (1927) when using potentials of the order of 40,000 volts per cm.; in these circumstances an ion moves at a speed of about 20 cms. per sec., and so travels many times the thickness of the ion atmosphere (*circa*  $10^{-8}$  cm.) in the time of relaxation ( $10^{-7}$ — $10^{-8}$  sec.). The unsymmetrical ion atmosphere can hardly ever be built up, and so the conductance approaches the value at infinite dilution (Joos and Blumentritt, 1927). The unusual increase of conductance of an electrolyte with high-frequency currents or high voltages is certainly not explicable on the basis of the Arrhenius theory of electrolytic dissociation, but the results are in conformity with the modern developments of that theory.

## REVIEW OF THE ELECTROLYTIC DISSOCIATION THEORY

If it were possible to draw a clear line between strong and weak electrolytes, then it might be assumed that all substances in the former category were completely ionised, and the inter-ionic attraction theory applied to account for the departure from ideal behaviour. In the latter category un-ionised molecules and ions would be assumed to exist in an equilibrium, to which the law of mass action is applicable. Unfortunately this sharp division is not possible; there are, for example, weak acids like acetic acid obeying the Ostwald law at reasonable concentrations but not in concentrated solutions; then there are the transition electrolytes, *e.g.*, cyanoacetic acid, trichlorobutyric acid, obeying the law only at low concentrations, and finally the strong acids which may comply with the law at extreme dilutions. Even with salts there are gradations in properties; thus mercuric perchlorate is a good conductor, and considerably ionised in aqueous solution, whereas the nitrate, chloride and cyanide are poor conductors. The halides of trimethyl-tin are normally ionised as good conductors in aqueous solutions, but their conductance and ionisation is much



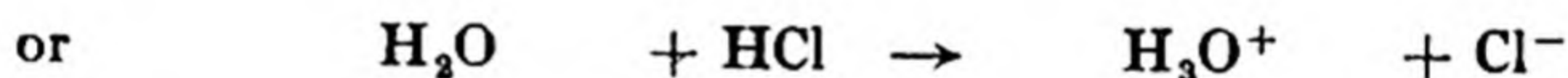
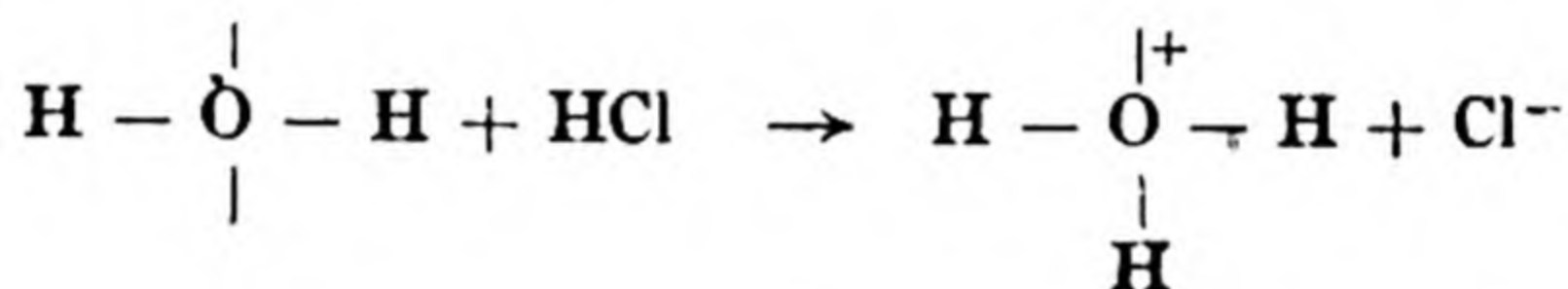
less in acetone, benzonitrile and nitrobenzene. Similarly the conductance measurements on tetraethylammonium iodide in various solvents, made by Walden (1906), have a marked range which does not appear explicable on the basis of the theory of complete ionisation.

The conclusion must be drawn, therefore, that electrolytes show a gradation of properties, and since some "strong" electrolytes definitely contain un-ionised molecules under certain conditions, it is not improbable that all electrolytic solutions contain such molecules. In most aqueous salt solutions, however, the proportion of these un-ionised or undissociated, or possibly "associated-ion," molecules is very much less than the value indicated by the conductance ratio. According to the latter a *N*-solution of hydrochloric acid should contain 15 per cent. of undissociated molecules, and should consequently have a very marked partial vapour pressure of hydrogen chloride; the actual value, although measureable, is very small, and so un-ionised molecules are present, but in a much lower proportion than anticipated from the original Arrhenius theory. Refractometric and light-absorption data (Fajans, 1927; von Halban, 1928) favour the view that even strong electrolytes contain a small proportion of "undissociated" molecules; the fraction undissociated, or of associated ions, is not more than 5 per cent. in solutions of concentration up to about 5*N*. The factors tending to cause an increase in the proportion of undissociated molecules or of associated ions are just those which are responsible for the tendency of an electrovalency to pass over into a covalency (p. 21), and so the relative sizes and charges of cation and anion must be considered in deciding on the possibility of partial dissociation.

In reviewing the evidence it appears, therefore, that even strong electrolytes may contain a small proportion of "undissociated" molecules, using the word in its most general sense to include covalent molecules and associated ions; in dilute solutions, however, ionisation may be considered to be complete for salts in solutions of fairly high dielectric constant, and the Debye-Hückel equations are applicable.



**Influence of Solvent.** There is no doubt that the degree of dissociation of an electrolyte is affected by the dielectric constant of the medium, since the constant determines the magnitude of the electrostatic force between the ions, but this cannot be the only factor operative. Kendall (1917 *et seq.*) has advanced evidence in support of the view that compound formation between solvent and solute is a preliminary to ionisation; although it is not certain that a definite compound must form, it is probable that the power of the solvent to donate to, or accept electrons from, the ions of the electrolyte is an important factor in ionisation. Pure hydrogen chloride and pure water are both almost non-conductors, but a mixture of the two is an excellent conductor; there seems very good reason to believe that the strong electron donating power of the oxygen in water results in the addition to it of a proton, thus



and the resulting mixture of  $\text{H}_3\text{O}^+$  and  $\text{Cl}^-$  is a good conductor.

Recent work on the dissociation of electrolytes has shown that solvents may be divided into two categories; the hydroxylic, or "levelling," solvents in which most salts behave as strong electrolytes, and the non-hydroxylic, or "differentiating," solvents, *e.g.*, nitromethane, acetonitrile and acetone, in which there is a considerable variation of behaviour. Hartley and his co-workers (1980 *et seq.*) suggest that since the hydroxyl group, of the hydroxylic solvent, has both electron donating and accepting properties it is able to attach itself by covalent linkages to both anion and cation; the protective sheath formed in this way prevents the ions from becoming "associated" as ion-pairs in the manner discussed above. The fact that most electrolytes are dissociated to a very large extent in hydroxylic solvents is thus accounted for. In the other category the solvent molecules are generally electron donors and can co-ordinate only with the



cations, leaving the anions unsolvated; under these conditions the ions are able to approach so closely that they become associated and are without electrical effect. This explains why some salts, *e.g.*, lithium and sodium thiocyanates, which are strong electrolytes in methyl alcohol (D.C. 30.3) are weak electrolytes in acetonitrile (D.C. 86), although a consideration of the dielectric constants alone would lead one to expect a small effect in the opposite direction. The results obtained by Hartley and his co-workers thus bring out in a very definite manner the influence of the solvent on the extent of dissociation or, more accurately, on the prevention of ion-association. A complete theory of electrolytes must take this important factor into consideration.

## REFERENCES

- BELL. *Ann. Reports*, 1934, 31, 58\*.
- BJERRUM. *Z. physikal. Chem.*, 1923, 104, 406; *Trans. Faraday Soc.*, 1927, 23, 445; *Ber.*, 1929, 62, 1091.
- BLAYDEN and DAVIES. *J. Chem. Soc.*, 1930, 949.
- BLUMENTRITT. *Ann. Physik*, 1928, 85, 812; 1929, 1, 195.
- BRØNSTED. *J. Amer. Chem. Soc.*, 1922, 44, 938; 1924, 46, 555; 1928, 50, 1338; *Trans. Faraday Soc.*, 1927, 23, 416\*.
- COATES. *Ann. Reports*, 1925, 22, 27\*.
- COATES and BUTLER. *Ibid.*, 1926, 23, 21\*.
- COWPERTHWAIT. *Trans. Faraday Soc.*, 1933, 29, 593.
- DAVIES *et al.* *Trans. Faraday Soc.*, 1927, 23, 351; 1931, 27, 621; *J. Chem. Soc.*, 1930, 2410, 2421; "The Conductivity of Solutions," 1933\*.
- DEBYE and FALKENHAGEN. *Physikal. Z.*, 1928, 29, 121, 401.
- DEBYE and HÜCKEL. *Physikal. Z.*, 1923, 24, 185, 305, 334; 1924, 25, 97, 145; *Rec. trav. chim.*, 1923, 42, 597; *Trans. Faraday Soc.*, 1927, 23, 334\*.
- FALKENHAGEN *et al.* *Z. physikal. Chem.*, 1929, 6B, 159; *Rev. Mod. Physics*, 1931, 3, 412\*; *Phil. Mag.*, 1932, 14, 537; "Electrolytes," 1934\* (English translation).
- FUOSS. *Trans. Faraday Soc.*, 1934, 30, 967; *J. Amer. Chem. Soc.*, 1934, 56, 1027, 1031, 1857; 1935, 57, 488; *Chem. Reviews*, 1935, 17, 27\*.
- FUOSS and KRAUS. *J. Amer. Chem. Soc.*, 1933, 55, 476, 1019, 2387, 3614; 1935, 57, 1.
- GLASSTONE. "The Electrochemistry of Solutions," 1930\*.
- HARTLEY *et al.* *Ann. Reports*, 1930, 27, 826\* (for very full references); *J. Chem. Soc.*, 1930, 2488, 2492; 1931, 199; *Proc. Roy. Soc.*, 1931, 132A, 427; *Chem. and Ind.*, 1931, 50, 807.
- HÜCKEL. *Physikal. Z.*, 1925, 26, 93.
- HUNT and BRISCOE. *J. Physical Chem.*, 1929, 33, 190, 1495.
- HUNTER. *Ann. Reports*, 1927, 24, 22\*.
- JONES *et al.* *J. Amer. Chem. Soc.*, 1933, 55, 62; 1935, 57, 2041.
- JOOS and BLUMENTRITT. *Physikal. Z.*, 1927, 28, 886.
- JOY and WOLFENDEN. *Proc. Roy. Soc.*, 1931, 134A, 413.



- KRAUS *et al.* *J. Amer. Chem. Soc.*, 1933, 55, 21 ; 1934, 56, 511, 2017, 2265 ; *Trans. Faraday Soc.*, 1935, 31, 749 ; *J. Chem. Ed.*, 1935, 12, 567\* ; *Trans. Electrochem. Soc.*, 1934, 66, 885\*.
- LA MER *et al.* *Trans. Amer. Electrochem. Soc.*, 1927, 51, 507\* ; *J. Amer. Chem. Soc.*, 1927, 49, 410 ; 1928, 50, 2656 ; 1929, 51, 2622, 2682 ; *Physikal. Z.*, 1928, 29, 558 ; *J. Phys. Chem.*, 1931, 35, 1958, 2245.
- LANGE *et al.* *Z. Elektrochem.*, 1930, 36, 1772 ; *Z. physikal. Chem.*, 1930, 148, 97 ; 1932, 160, 445 ; *Chem. Reviews*, 1931, 9, 89\* ; *J. Amer. Chem. Soc.*, 1932, 54, 8120.
- LEWIS and RANDALL. *Ibid.*, 1921, 43, 1112 ; "Thermodynamics," 1923\*.
- LOWRY. *Trans. Faraday Soc.*, 1927, 23, 508 ; 1928, 24, 1.
- MACINNES. *J. Amer. Chem. Soc.*, 1921, 43, 1287 ; *Chem. Reviews*, 1933, 13, 29\*.
- MARTIN. *J. Chem. Soc.*, 1928, 3270 ; 1930, 580.
- MILNER. *Phil. Mag.*, 1912, 23, 551 ; 1918, 25, 742.
- NOYES *et al.* *J. Amer. Chem. Soc.*, 1924, 46, 1080, 1098 ; 1925, 47, 2122 ; 1926, 48, 621.
- ONSAGER. *Physikal. Z.*, 1926, 27, 388 ; 1927, 28, 278 ; *Trans. Faraday Soc.*, 1927, 23, 341 ; *Chem. Reviews*, 1933, 13, 78\*.
- RANDALL. *Trans. Faraday Soc.*, 1927, 23, 502.
- RANDALL and SCOTT. *J. Amer. Chem. Soc.*, 1927, 49, 647.
- REDLICH and ROSENFELD. *Z. physikal. Chem.*, 1931, 155, 65.
- ROBINSON. *J. Physical Chem.*, 1928, 32, 1089 ; 1929, 33, 1193 ; *J. Amer. Chem. Soc.*, 1932, 54, 1811.
- SACK. *Physikal. Z.*, 1928, 29, 627 ; 1929, 30, 576.
- SCATCHARD. *J. Amer. Chem. Soc.*, 1925, 47, 641 ; *Physikal. Z.*, 1932, 33, 22 ; *Chem. Reviews*, 1933, 13, 7\*.
- SCHINGNITZ. *Z. Elektrochem.*, 1930, 36, 861\*.
- SEWARD *et al.* *J. Amer. Chem. Soc.*, 1930, 52, 8692 ; 1932, 54, 554.
- THOMPSON. *Ann. Reports*, 1931, 28, 31\*.
- WIEN. *Ann. Physik*, 1927, 83, 327 ; 1928, 85, 895 ; *Physikal. Z.*, 1927, 28, 834.
- WILLIAMS. *J. Amer. Chem. Soc.*, 1929, 51, 1112 ; *Chem. Reviews*, 1931, 8, 308\*.
- WILLIAMS and FALKENHAGEN. *Z. physikal. Chem.*, 1928, 137, 399 ; *J. Physical Chem.*, 1929, 33, 1121.
- WOLFENDEN. *Ann. Reports*, 1932, 29, 21, 29\*.
- WYNNE-JONES. *J. Chem. Soc.*, 1930, 1064 ; 1931, 795.
- ZAHN. *Z. Physik.*, 1929, 58, 470.

\* Review papers and books, wherein further references are to be found, are marked by an asterisk.



# INDEX

- Acceptor**, of electrons, 16, 31, 37
- Acetaldehyde**, photochemical oxidation, 335  
thermal decomposition, 407
- Acids**, strength of, 26
- Activation**, heat, or energy of, 262–302  
and reaction velocity, 265, 266, 271  
calculation of, 267, 275  
in atomic reactions, 272  
in bimolecular reactions, 262 *et seq.*  
in heterogeneous reactions, 429  
in termolecular reactions, 281–283  
in unimolecular reactions, 297  
origin of, 264, 269, 297  
theoretical calculation, 275
- Active centres of catalytic surfaces**, 416–423
- Activity**, coefficient, 440–460  
calculation of, 452–457  
determination, 443–450  
of individual ions, 448  
concept, 439  
definition, 440
- Adhesional work**, 347
- Adsorption**, 378–393  
activated, 388  
and catalysis, 394, 424, 426–429  
chemical, 379, 391  
forces, 380  
Gibbs' equation, 350, 373  
Langmuir equation, 382  
limiting, 352, 384  
of atoms, 426  
of gases, 378  
of solutes, 350–353  
physical, 379, 388
- Aldehydes**, photolysis, 333–334
- Alkali metals**, co-ordination compounds, 46
- Amine oxides**, 33
- Ammines**, structure of, 39–43
- Ammonia**, catalytic decomposition, 405, 427, 429  
molecular structure, 153  
photochemical decomposition, 332
- Ammonium ion**, 39
- Arrhenius equation**, 262, 265, 298
- Association**, 48  
and parachor, 123  
of dipoles, 137  
of hydroxy-compounds, 48, 95, 124
- Atomic reactions**, 272  
structure, 1–9
- Atoms**, recombination of, 284  
"Aufbauprinzip," 81
- Azoxy-group**, structure, 113
- Band spectra**. *See* Molecular Spectra.
- Bases**, strength of, 49
- Benzene**, structure of, 88, 110, 250
- Bimolecular films**, 381
- Bimolecular reactions**, 261–280  
one reacting substance, 261  
two reacting substances, 270
- Birge and Spenser method**, for heats of dissociation, 226, 239  
sources of error, 228
- Bivalent hydrogen**. *See* Hydrogen, co-ordinated.
- Bohr-Bury theory**, 3
- Bohr theory of spectra**, 5, 56
- Boiling point and semi-polar bonds**, 34  
and electrovalency, 23
- Boron hydride**, 31, 68
- Bromine**, dissociation of, 222
- Carbon**, atom, excited state, 67, 71  
stereochemistry, 61, 138  
dioxide, structure, 150  
isotopes, 236  
monoxide, structure, 18, 91  
by dipole moment, 177  
by parachor, 115  
by Raman effect, 254  
-chlorine reaction, 337



- Carbonyls**, structure, 43-45
- Catalysis** and molecular distortion, 423  
     heterogeneous, 394-437  
     intermediate compound theory, 433  
     negative, 314
- Catalytic**, reactions, complexity, 396  
     mechanism, 397  
     order of, 399  
     retardation by products, 402-408, 415  
     retardation by reactants, 411-415  
     with single gas, 398  
     with two gases, 408  
     surfaces, active centres, 416-425  
     uniformity, 420
- Chain reactions**, 291, 302-314, 335-344  
     and negative catalysis, 314  
     and unimolecular reactions, 291, 307  
     critical pressure limits, 309  
     energy, 302  
     evidence for, 304  
     in photochemical processes, 323, 335-344  
     in various oxidation processes, 308, 310  
     kinetics, 308  
     material, 303  
     non-stationary, 309  
     originating at surfaces, 311  
     stationary, 308
- Chelate compounds**, 44  
     and parachor, 116
- Chemisorption**, 379, 391
- Chlorine**, dissociation of, 222  
     isotopes and band spectra, 196, 208, 246
- Cohesional work**, 348
- Collisions**, molecular, effective, 265, 268, 270, 281  
     in atomic reactions, 272  
     in bimolecular reactions, 265  
     in termolecular reactions, 281  
     in unimolecular reactions, 297
- Compound formation** and dipole moment, 180
- Condensed films**, 357
- Conductance**. *See* Electrolytic Conductance.
- Conductance ratio**, 438
- Configuration theory**, 81
- Continuous spectra**, 220
- Co-ordinated hydrogen**. *See* Hydrogen.
- Co-ordinate link**, or valency, 17, 36-52.  
     *See also* Semi-polar linkage.
- Co-ordination compounds**, 39-47, 72  
     numbers, odd, 58
- Covalency**, 14, 27-30, 66  
     maximum, 52
- Critical potential**, 184  
     pressure limits, 309  
     solution temperature, 50  
     temperature of surface films, 395
- Crystal structure**, 19, 450
- Dative bond**, 16
- Debye-Hückel theory**, 452-461  
     tests of, 457-460
- Deuterium**, 236  
     -oxygen reaction, 314
- Diazo-group**, structure, 112
- Dielectric constant**, 127  
     and activity coefficient, 455  
     and conductance, 466  
     and dipole moment, 134  
     and dissociation, 468  
     and ion-association, 464  
     and molecular radius, 131  
     and polarisation, 128, 131  
     and refractive index, 129  
     and semi-polar bonds, 35
- Diketones**, metallic derivatives, 45, 116  
     structure of  $\alpha$ -, 112  
     structure of  $\beta$ -, 118, 120
- Dipole induced**, 128, 156, 159, 162-3  
     moment, 133-180  
         additivity, 156  
         and association, 136  
         and compound formation, 180  
         and free rotation, 169-175  
         and molecular structure, 149-153, 175-180  
         allene system, 177  
         ammonia, 127  
         carbon dioxide, 124  
         carbon monoxide, 149  
         *cis-trans* configurations, 178  
         *iso*-cyanides, 175  
         nitrous oxide, 151  
         water, 151  
         and partially restricted rotation, 172  
         and restricted rotation, 174, 175  
         and semi-polar bonds, 180-181  
         and solvent effect, 144-149



- Dipole moment and tautomeric effect**, 164  
 and valency angles, 178-180  
 determination of, in dilute solutions, 142  
 molecular beam method, 141  
 refraction method, 139  
 temperature method, 138  
 in homologous series, 155  
 of alcohols, 156  
 of esters, 174  
 of ethylene derivatives, 161  
 of groups, 156-161  
 of linkages, 160  
 of nitrogen derivatives, 168  
 of oxygen derivatives, 166  
 of salts, 154  
 results, 150  
 sign of, 158  
 vector addition, 158, 160
- Dissociation and continuous spectra**, 220-226  
 and pre-dissociation spectra, 231  
 and Raman spectra, 254  
 constant, 438-442  
 of bases, 48  
 electrolytic. *See* Electrolytic Dissociation.  
 heat of, 220-232, 238, 255
- Distortion of electronic fields**, 153  
 and catalysis, 423  
 and valency, 21  
 of groups, 159  
 of molecules and catalysis, 423  
 polarisation. *See* Polarisation.
- Donor of electrons**, 16, 32, 37
- Double halide**, 38  
 "Dreierstoss," 285
- Dupré's equation**, 347
- Effective atomic number**, 42-44
- Eigenfunction**, 56
- Eigenvalue**, 56
- Einstein's law of photochemical equivalence**, 319-323, 325  
 apparent exceptions, 323, 324  
 conditions of applicability, 322
- Electrolytes**, gradation of, 466  
 strong, 438 *et seq.*
- Electrolytic conductance**, 19-23, 461  
*et seq.*  
 and complete ionisation, 461  
 and electrovalency, 19-20  
 and Fajans theory, 21-23  
 at high frequencies, 465  
 influence of solvent, 468  
 with high voltages, 465  
 dissociation theory, 450  
 review, 466
- Electron**, 1  
 and waves, 1, 54  
 bonding and anti-bonding, 81 *et seq.*  
 charge density, 64  
 donor, 16, 33, 37  
 eigenfunction. *See* Orbital.  
 octet, 13  
 orbital. *See* Orbital.  
 pairs, 13, 66  
 promoted, 81  
 sextet, 30, 36  
 spins, 7 *et seq.*  
 wave function. *See* Orbital.
- Electronic, arrangement in atoms**, 1-9  
 in stable complexes, 39-44  
 band spectra, 182, 188, 210 *et seq.*  
 and heat of dissociation, 220  
*et seq.*  
 cause of head, 213  
 isotope effect in, 232  
 molecular dimensions from, 214  
 configuration, of atoms, 9  
 of molecules, 10, 79-81  
 of "united atoms," 10  
 energy levels, 184  
 states, 9  
 theory of valency, 12 *et seq.*  
 transitions, 186
- Electrovalency**, 14, 18-25
- Energy, change in electronic transitions**  
 185  
 in rotational transitions, 188  
 in vibrational transitions, 188  
 levels, 184-187  
 "pass," 278, 279, 432  
 sub-levels, 186
- Equilibrium vibration frequency**, 199, 245
- Ethylene-hydrogen reaction**, 410
- Exchange energy**. *See* Resonance.
- Expanded films**, 364-368, 371  
 liquid and vapour, 365
- Fajans theory**, 21, 22, 25, 154
- Franck-Condon principle**, 219



- Free radicals and unimolecular reactions**, 307
- Fundamental bands**, 200  
in solids, 241, 242
- Gas reactions**, heterogeneous, 394 *et seq.*  
homogeneous, 260 *et seq.*
- Gaseous films**, 366, 368, 373  
of soluble substances, 373-378  
two-dimensional, 368
- Gases**, adsorption of, 378-391  
stable films, 379  
two-dimensional, 387
- Gibbs' adsorption equation**, 350, 373-378
- Heat of activation**. *See* Activation.  
of dissociation. *See* Dissociation.
- Heitler and London method**, 57  
applications, 60-63, 68-75  
theory of valency, 66
- Heterogeneous gas reactions**, 395 *et seq.*
- Homogeneous gas reactions**, 260 *et seq.*  
bimolecular, 261  
termolecular, 280  
unimolecular, 286
- Homopolar method in wave mechanics**.  
*See* Heitler-London.
- Hydrogen**, -bromine reaction, 338  
-chlorine reaction, 303, 341  
co-ordinated, 38, 47-52  
and resonance, 93-96  
duality of, 25  
fluoride complexes, 47  
heat of dissociation, 63, 227  
iodide, decomposition,  
heterogeneous, 427  
homogeneous, 261  
photochemical, 322  
formation, 271  
ion, 26, 468  
isotope of, 210, 236  
molecule, Heitler - London  
treatment, 60-64  
ion, 31, 68  
orbital treatment, 75-78  
states of, 64, 76  
negative, 27  
ortho-para conversion, 279, 426  
-oxygen reaction, 413 *et seq.*
- Hydroxyl compounds**, association, 48, 95, 124
- Inert gases**, structure, 3, 4
- Infra-red spectra**, 191 *et seq.*
- Intermediate compound theory of catalysis**, 433
- Iodine**, dissociation of, 222
- Ion**, activity coefficients, 449
- Ion-association theory**, 464-465
- Ionic strength**, 446, 455
- Ionisation**, complete, 450
- Isocyanide group**, structure by dipole moments, 175  
by parachor, 114  
by Raman spectrum, 251
- Isosteres**, 29
- Isotopes**, effect in electronic spectra, 232  
in Raman spectra, 246  
in rotational spectra, 196  
in vibrational spectra, 207  
of carbon, 236  
of chlorine, 196, 208, 246  
of hydrogen, 210, 236  
of nitrogen, 236  
of oxygen, 232-235
- Keto-esters**, 51, 94
- Ketones**, photolysis, 333-335
- Kinetics of bimolecular reactions**, 261 *et seq.*  
of chain reactions, 308  
of photochemical reactions, 335 *et seq.*  
of termolecular reactions, 280-286  
of unimolecular reactions, 286 *et seq.*
- Kossel's theory**, of valency, 12
- Langmuir's theory**, of adsorption, 378  
of electronic arrangement, 2
- Lewis' theory**, of valency, 13
- Lindemann's theory**, of unimolecular reactions, 292
- Lone pairs**, of electrons, 28, 32
- Long chain molecules**, 247 *et seq.*
- Lorentz-Lorenz equation**, 129
- Macleod's equation**, 98
- Maxwell's distribution law**, 264
- Melting point and electrovalency**, 24
- Milner's theory**, of electrolytes, 451
- Mobility in surface films**, 385
- Molecular**, beams, 141, 387, 432  
compounds, 36  
and dipole moment, 180



**Molecular configuration and wave mechanics**, 74, 79  
 dimensions in films, 352, 358, 376  
 orbitals. *See* Orbitals.  
 radius and dielectric constant, 131  
 and spectra, 195, 205, 214  
 spectra, 183 *et seq.*  
 and molecular constants, 193, 205, 214  
 and photochemical reactions, 326 *et seq.*  
 electronic. *See* Electronic band spectra.  
 isotope effects in. *See* Isotopes.  
 of gases, 191 *et seq.*  
 of liquids, 236  
 of solids, 240  
 rotational. *See* Rotational spectra.  
 types of, 187  
 vibrational. *See* Vibrational spectra.  
**Moment of inertia**, from spectrum measurements, 195, 205, 214  
**Morse equation**, 266, 276  
**Mosotti-Clausius equation**, 127, 128, 133  
  
**Negative catalysis**, 314  
**Nitrogen**, glow of active, 286  
 isotopes, 236  
 molecular orbitals, 81  
 pentoxide, decomposition, 286  
 valency angle, 71, 72  
**Nitro-group**, dipole moment, 157  
 structure of, 34  
 by parachor, 113  
 symmetry of, 34, 92, 168  
**Nitroso-group**, structure of, 112  
**Nitrosyl chloride**, decomposition, 330  
 formation, 284  
**Nitrous oxide**, decomposition, 269, 301-302  
  
**Octet**, electron, 13  
 not a maximum, 30  
 tetrahedral arrangement, 28, 71  
**Odd electron linkage**. *See* Singlet linkage and Three-electron linkage.  
**Onsager's equation**, 463  
**Orbitals**, and hydrogen molecule, 75  
 and resonance, 90  
 and valency, 95-97

**Orbitals**, definition of, 56  
 method of atomic, 58, 59. *See also* Heitler-London.  
 of molecular, 58, 59, 75-87  
**Orientation polarisation**. *See* Polarisation.  
**Ostwald's dilution law**, 438  
**Overtone**s in vibrational spectra, 200, 201  
**Oxy-acids**, 35  
**Oxygen**, heat of dissociation, 228, 232  
 isotopes, 232-236  
 molecule, configuration, 83-85  
 photochemical ozonisation, 330  
 symmetrical and unsymmetrical forms, 235  
 valency angle, 70, 74, 152, 179, 180  
  
**Parachor**, 98 *et seq.*  
 additivity, 100  
 and covalency increase, 119  
 and semi-polar linkage, 105  
 and singlet linkages, 115-123  
 anomalies, 105-107  
 applications, 110-115  
 as a molecular volume, 99  
 defects, 121  
 definition of, 99  
 equivalents, 102, 103  
 of associated liquids, 123  
 of elements, 124  
 of mixtures, 107-110  
 of organo-metallic compounds, 106, 116  
 strain constants, 105  
**Paraldehyde**, structure, 111  
**Pauli's exclusion principle**, 7, 12, 64, 77  
**P-branch** in electronic spectra, 214  
 in vibrational spectra, 201  
**Phenolic derivatives**, parachors of, 119  
**Photochemical**, decomposition, of  
 aldehydes, 333  
 of ammonia, 332  
 of hydrogen iodide, 328  
 of ketones, 333  
 of nitrosyl chloride, 330  
 equivalence law, 319  
 conditions of applicability, 322  
 evidence for, 325  
 reactions, 328 *et seq.*  
 and molecular spectra, 326-335  
 kinetics of, 335-344  
**Platinic ammines**, 42  
**Platinous ammines**, 39



- Polar, groups and spreading, 348**  
     moments. *See* Dipole moments.  
     properties, 34  
     and boiling point, 34  
     and dielectric constant, 35
- Polarisability, 128**
- Polarisation, atom, 130, *et seq.*, 141**  
     distortion, 128 *et seq.*  
     electron, 180 *et seq.*  
     and physical state, 136  
     molar, 129  
     orientation, 133 *et seq.*  
     and physical state, 135  
     total, 134  
     and physical state, 135  
     of mixtures, 142
- Potential energy curves, 62, 216-220, 224, 230**  
     and dissociation, 225  
     and pre-dissociation, 230
- Pre-dissociation spectra, 229**  
     and heat of dissociation, 231  
     and photochemical reactions, 332
- Pressure limits, of explosions, 309**
- Probability factor, 274**
- Q-branch, in electronic spectra, 212**  
     in Raman spectra, 247  
     in vibrational spectra, 203
- Quantisation of molecular energy, 184**
- Quantum, efficiency, 320**  
     abnormal, 323, 324  
     and wavelength, 325  
     groups, 6  
     mechanics. *See* Wave mechanics.  
     mechanism of reactions, 322  
     number and wave mechanics, 56  
     of electrons, in atoms, 6  
     in molecules, 10, 80
- Quinone, structure, 111**
- Radiation theory and unimolecular reactions, 289**
- Raman effect, 243 *et seq.***  
     and ionisation, 251  
     and molecular rotation, 246  
     and molecular structure, 251  
     and molecular vibration, 244  
     and strength of linkages, 252-256  
     electronic transition, 249  
     of linkages, 249 *et seq.*  
     of organic compounds, 249
- Raman effect, of salts, 256**  
     Q-branch in, 247
- R-branch, in electronic spectra, 213, 214**  
     in vibrational spectra, 201-203
- Reaction velocity constant, and temperature, 262, 266**  
     calculation of, 267, 275
- Refraction, molar, 129**  
     and physical state, 136
- Refractive index, and dielectric constant, 129**  
     and electron polarisation, 130  
     for long waves, 130
- Resonance and association, 95**  
     and co-ordinated hydrogen, 93-96  
     and heat of formation, 91  
     and inter-atomic distances, 90  
     and parachor, 111, 124  
     defined, 88  
     energy, 61, 68, 69, 74, 86, 89  
     in benzene, 88  
     in boron hydride, 31, 68  
     in carbonate ion, 92  
     in carbon dioxide, 92  
     in carbon monoxide, 91  
     in hydrogen molecule, 61  
     in nitrate ion, 92  
     in nitro-group, 92  
     in odd-electron bonds, 68
- Restoring force, from Raman effect, 253**  
     in hydrogen halides, 207
- Rotational, energy levels, 186 *et seq.***  
     multiplicity, 197-198  
     energy of molecule, 192  
     quantum number, 187, 192  
     separation in vibrational bands, 202  
     spectra, 191 *et seq.*  
     and molecular dimensions, 194  
     isotope effect in, 196  
     transitions, 190
- Scattering of light, 243**
- Schrödinger's equation, 55**
- Semi-polar linkage, 16-18**  
     and parachor, 105  
     and polar properties, 34  
     stereochemistry of, 36
- Sextet of electrons, 30, 36**
- Single electron linkage. *See* Singlet linkage.**
- Singlet linkage, 30, 32**  
     and the parachor, 115-123  
     and wave mechanics, 68, 86, 95
- Solubility and electrovalency, 25**



- Solvent and dipole moment**, 144-148  
in electrolytic dissociation, 468
- Spectra**, atomic, 5  
continuous, 220  
multiplicity, 10, 66  
of gases, 183 *et seq.*  
of linkages, 237-240  
of liquids, 236  
of solids, 240  
*See also* Electronic, Molecular, Pre-dissociation, Raman, Rotational and Vibrational Spectra.
- Spectroscopic term formulæ**, atomic, 9  
molecular, 11
- Spreading, and polar groups**, 348  
coefficient, 347  
of oils, 346
- Stereochemistry, and wave mechanics**, 70-75  
of semi-polar linkage, 36
- Sulphur, stereochemistry**, 36  
valency angle, 70, 179, 180
- Surface films**, 354 *et seq.*  
condensed, 357  
expanded, 364, 371  
gaseous, 366, 368, 373-378  
mobility in, 385  
of soluble substances, 350, 373  
potentials of, 370-373  
solid and liquid, 363
- Surface pressure**, 377
- Surface tension, and adsorption**, 350-354  
and molecular orientation, 351  
and parachor, 99  
and spreading of oils, 346
- Temperature, and reaction velocity**, 262, 266
- Termolecular reactions**, 280-286  
mechanism of, 283
- Ternary collisions**, 281
- Thallium compounds, parachors of**, 117
- Three-body collisions**, 284, 337, 339
- Three-electron linkage**, 69, 87
- Tilt of molecules, in films**, 364
- Transition state theory**, 274
- Triazo-group structure**, 112
- Triple ions**, 464
- "Tunnel" effect**, 279, 433
- Unimolecular films**, 350 *et seq.*  
of gases, 380
- Unimolecular films, of insoluble substances**, 350, 354 *et seq.*  
of soluble substances, 353, 373 *et seq.*
- Unimolecular reactions**, 286-302, 307  
activation energy, 297  
and bimolecular reactions, 301  
and free radical chains, 307  
chain theory of, 291  
collision theory of, 292 *et seq.*  
degrees of freedom, 298  
effect of hydrogen molecules, 296  
effect of pressure, 293  
mechanism of, 289 *et seq.*  
molecular collisions in, 297  
radiation theory of, 289
- Valency, and spectral multiplicity**, 66  
and unpaired electron spins, 66  
angles, 70, 74, 152, 178  
*See also* Co-ordinate, Covalency, Electronic theory, Electrovalency, Semi-polar, Singlet and Three-electron linkages.
- Van der Waals adsorption**, 379, 388-390
- Velocity of reaction. See Reaction.**
- Vibrational bands, energy levels**, 186-188  
energy of molecules, 199  
fundamental and overtones, 200  
quantum number, 187, 199  
spectra, 199  
and isotopes, 207  
and molecular dimensions, 204  
transitions, 189
- Vibrations, anharmonic**, 200, 215, 226  
in the carbonate group, 241  
in the nitrate group, 255  
in the sulphate group, 242, 256
- Water, association of**, 48, 124  
molecular structure, 70, 74, 151
- Wave functions, complete**, 64  
electron. *See* Orbitals.
- Wave mechanics**, 53 *et seq.*  
and catalysis, 433  
and stereochemistry, 70-75, 79  
and the covalent bond, 66  
and the hydrogen molecule, 60-66, 75-78  
and the singlet linkage, 68, 86
- Werner's theory of valency**, 39